

## **Appendix H**

### **Overcoming Operational Challenges in Sour Water Stripping**

# OVERCOMING OPERATIONAL CHALLENGES IN SOUR WATER STRIPPING

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Sour Water Strippers (SWS) are used primarily to remove  $\text{NH}_3$  and  $\text{H}_2\text{S}$  from refinery waste water streams. As with any industrial process, there are challenges to keeping a Sour Water Stripper (SWS) unit on-stream and on-specification between shutdown periods. These challenges can be grouped as follows:

- Limiting fouling
- Maintaining treated water ammonium ( $\text{NH}_4^+$ ) and total sulphur specification
- Managing corrosion
- Limiting hydrocarbon content of the off-gas
- Managing feed water quality.

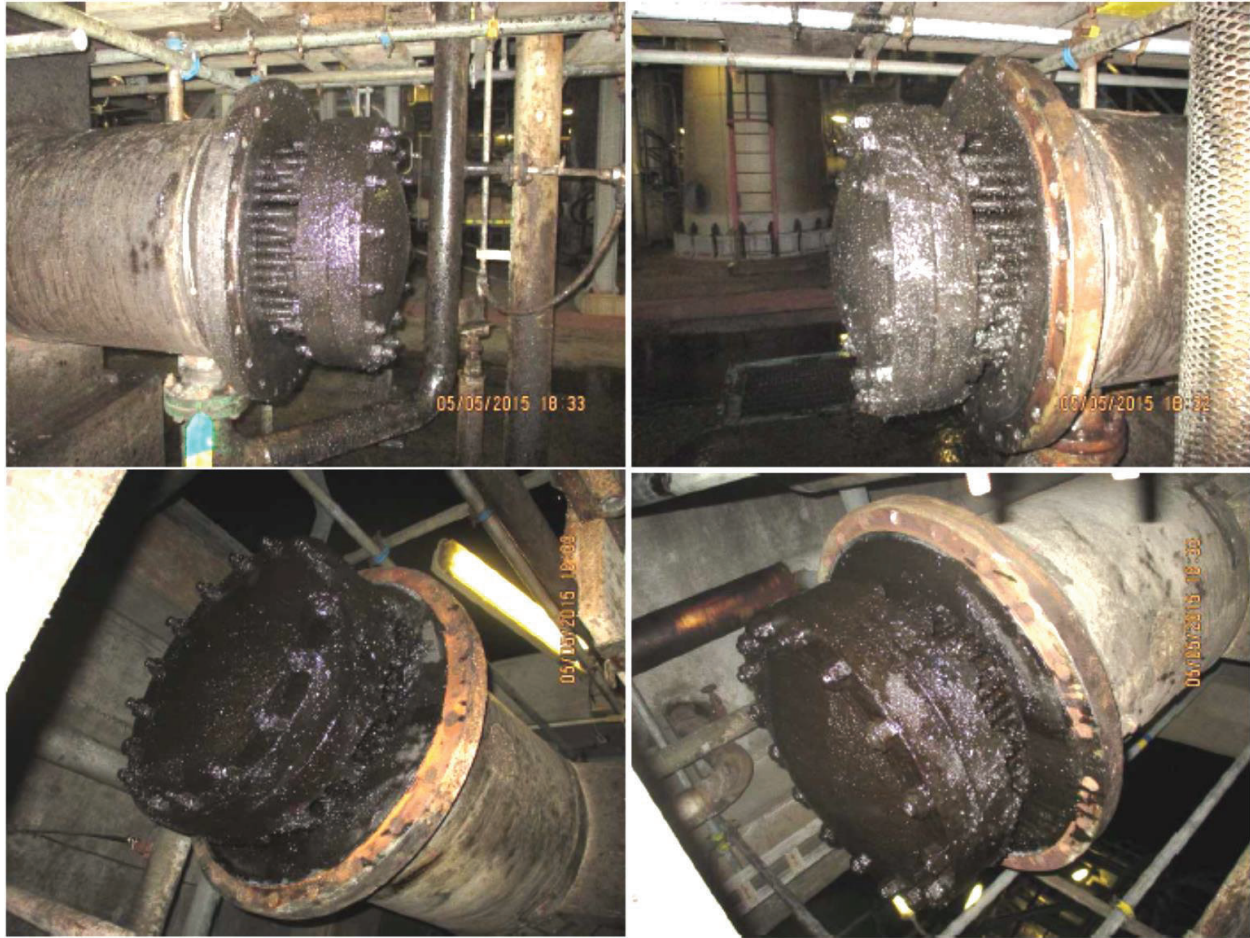
## Challenge 1: Fouling

Sour Water Stripping is considered “fouling service” and, thus, it is generally recommended that fouling-resistant trays be installed in the column. In some instances, improved run time has been achieved by replacing conventional trays with fouling-resistant trays (*Hauser and Kirkley, 2003*) and installing bypasses around individual feed/effluent exchangers (there are often several in series) to allow for on-stream cleaning.

There are several types of fouling that have been observed, historically, in SWS units and the nature of the fouling can broadly be divided into five categories:

- 1) Hydrocarbons
- 2) Particulates
- 3) Salts
- 4) Elemental Sulphur
- 5) Polymers

**Hydrocarbon**-based fouling often occurs when a large volume of naphtha and heavy boiling-range hydrocarbon material is carried into a sour water stripper. The hydrocarbon will tend to agglomerate to small particulates in the unit feed water or particulates generated by corrosion in the stripper. This tends to result in a sticky, black, sludge-like substance that frequently accumulates in the exchangers. A common example of this type of fouling is shown in Figure 1. A more gum-like texture is also possible and is often associated with heavy hydrocarbon wax fractions or cracked feeds entering the unit.



**Figure 1 Typical Hydrocarbon-Based Fouling of a SWS Feed/Effluent Exchanger**

This sort of fouling is the most prevalent in the industry. Mitigation is usually achieved by:

- 1) Improving maintenance and control on upstream water boots to prevent bulk carry-under of hydrocarbons with the sour water
- 2) Ensuring good control of the oil-water interface in the three-phase separator on the sour water feed (normally a liquid level of 50 to 60% is optimal)
- 3) Using appropriate technology to remove emulsified hydrocarbon (this can take the form of a long-residence time feed tank with skimming facilities or an inlet filter coalescer system). Some water-oil emulsions can take several days to separate into distinct phases so the separation can be challenging.
- 4) Periodically washing the column if sufficient storage capacity for sour water exists (normally 48 hours is required). Various procedures exist, often with multiple washes. Broadly weak acid and base washes are used to remove scaling (precipitated salts) with detergent washes (or in some cases, just as effectively, vapour phase naphthenic hydrocarbon with steam) being used to remove hydrocarbons.

The stability of a hydrocarbon emulsion can be strongly affected by pH. In a typical refinery SWS, the pH rises as the water passes down through the column (in the absence of un-neutralised strong-base contaminants) because hydrogen sulphide ( $H_2S$ ) is more readily stripped from the

sour water than ammonia ( $\text{NH}_3$ ). This effect can result in a hydrocarbon phase forming in the lower part of the stripper column and on the effluent side of a feed/effluent exchanger, preferentially fouling the effluent rather than the feed side of the feed/effluent exchanger.

**Particulate**-based fouling is normally a result of coke (from thermal cracking units), catalyst fines upstream corrosion products or corrosion products generated in the SWS unit. In many cases, this type of fouling is seen in conjunction with hydrocarbon or salt precipitation fouling as the particulate fines provide a nucleus for hydrocarbon agglomeration or salt crystallization. This type of fouling is usually mitigated by:

- 1) Locating the source of the particles and addressing the issues causing their generation
- 2) Filtering the feed water (while this is not always required, it is in some cases necessary, especially if the column is packed. Most conventional and high-performance packings can become plugged by high particulate loads.)

One example of the many possible variations of this fouling type is shown in Figure 2.



**Figure 2     Particulate-Based Fouling of a SWS Feed/Effluent Exchanger**

**Salt**-based fouling is typically a result of the presence of calcium or magnesium ions in the feed water to the stripper. To avoid this type of fouling, the water feed to the SWS should not have appreciable water hardness (a standard test for Ca and Mg). Typically, this sort of fouling occurs because of low-quality wash water, a problem with the refinery's water treatment plant, or an ingress of poor-quality water into the system (for example through a leaking water cooler on an upstream unit).

Sour water from coal gasification plants typically contains  $\text{CaCO}_3$  which requires a pH of 6 to 6.5 to prevent precipitation. Hydrochloric acid is typically used to adjust the water pH to the acceptable range. Unfortunately, the use of a strong acid often results in difficulty meeting ammonia specification in the treated water, thus the acid method should be avoided. Sulphuric acid should be avoided as it will result in sulphur forming side reactions with  $\text{H}_2\text{S}$ .

Selenium can precipitate out in a SWS column and is typically grey in colour (this form of selenium normally requires temperatures of  $180^\circ\text{C}$  /  $355^\circ\text{F}$ , but the presence of amine catalyzes its formation (*Greenwood and Earnshaw, 1997*)), as shown in Figure 3. It has also in some cases resulted in pink-coloured stripped water.



**Figure 3** Valve Fouled with Selenium

In some rare instances crude oils contain complex chemical scavengers, such as triazine, that can precipitate out of solution (Figure 4). The only prevention for this problem is to avoid adding these chemicals upstream.

While other salts are possible, generally they must be present at much higher concentrations to precipitate than are normally found at steady operating conditions. For example, if very large volumes of caustic enter the system this can create a salt precipitation problem, as seen in Figure 5 and should be kept out of the SWS feed as far as possible. SWS units are (generally) not suitable for treating caustic effluents.



**Figure 4** Overhead Condenser Fouled with Triazine



**Figure 5** Precipitation of Sodium Salts in a Pump

Ammonium carbonate and bicarbonate will sublime from the SWS off-gas in the temperature range of 55 to 75°C (130 to 167°F). When the gas cools excessively, this solid forms that fouls instruments, control valves and lines (Figure 6). A minimum gas temperature of 85°C should be maintained to prevent sublimation. Checking overhead lines for cold spots should be done on a regular basis. These lines should be insulated and steam traced as a minimum, but steam jacketing is preferred.



Figure 6 Sublimed Ammonium Carbonate/Bicarbonate Salts Fouling in a Pipe

**Elemental Sulphur** There are four known pathways for elemental sulphur to form in a SWS column:

- 1) Decay or overdosing of sodium/ammonium polysulphide (this is sometimes injected into SWS units to neutralize free cyanide). This component decays above 110°C/230°F and at a pH below 7. This problem can be avoided by adding the correct amount of polysulphide in an appropriate location. Figure 7 illustrates this type of sulphur formation.
- 2) 'Wet-Claus reaction'- requires oxygen and an acidic environment; conditions which are not present in most refinery SWS units. The problem of sulphur formation is avoided via preventing oxygen ingress.



- 3) Thiosulphate decomposition - requires an acidic environment that is not commonly found in refinery SWS units.



- 4) Sulfuric acid dosing - sulphuric acid can react with H<sub>2</sub>S to form elemental sulphur (see Figure 7).





**Figure 7** Left: Decayed Polysulphide Fouling in Reflux Water; Right: Elemental Sulphur in Sour Water after Sulphuric Acid Dosing

**Polymers** Reported fouling mechanisms from polymerisation in sour water stripping include:

- 1) Hydrogen Cyanide (HCN) self-polymerization
- 2) Amine degradation and oxidation products
- 3) Red oil
- 4) Peroxides
- 5) Olefins
- 6) Thiophenes/Thiophenols
- 7) Phenols and polyphenols

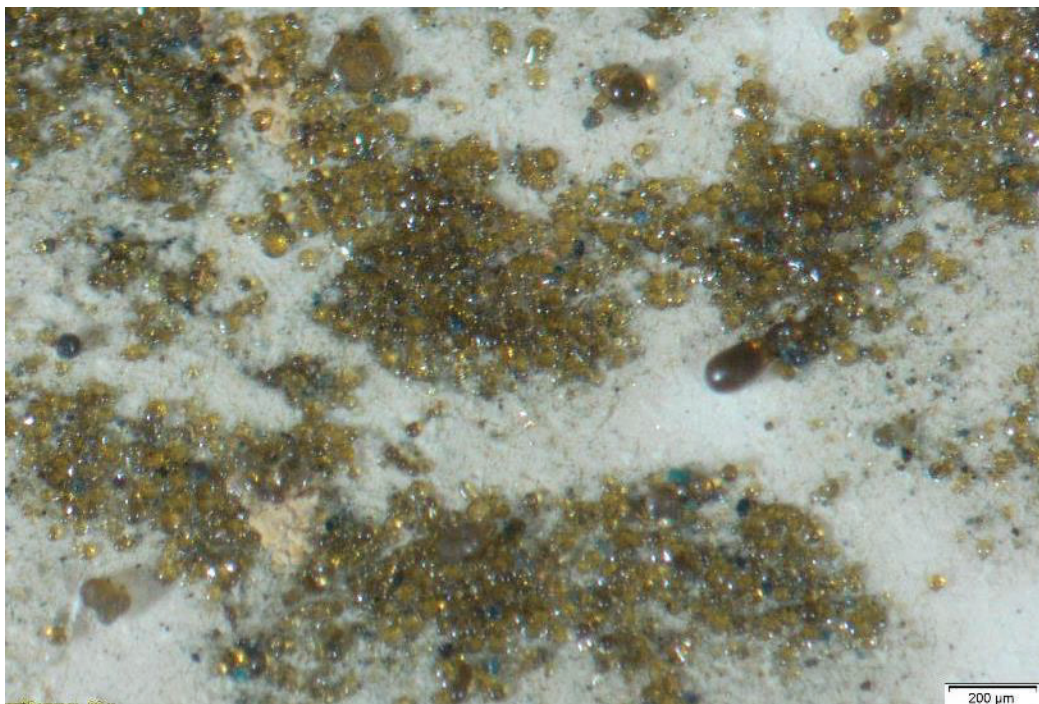
- 1) **HCN** can self-polymerize in an ammonia solution (*Matthews and Moser, 1967*). This has been reported to occur in the pH range 8.5 to 10.5 at 110°C with an HCN concentration above 0.02N. This is based on batch laboratory experiments and may occur over a somewhat different range of conditions in an actual stripper system.

Neutralisation of the HCN by the addition of ammonium or sodium polysulphide is the solution to this issue.

- 2) **Amine Degradation** and oxidation products have been reported as a precursor to fouling reactions. This is typically only an issue if there is a bulk flow of amine into a sour water system. Normal bleeds, washes, or purges with low levels of entrained amine are not an issue from a fouling perspective.

A healthy amine unit should have minimal amine in its reflux water system. Should amine fouling be an issue it is recommended to investigate upstream operation. Foaming of the amine regenerator should be resolved. In addition, the injection of amine-based corrosion inhibitors on other units should be examined.

- 3) **Red-Oil** fouling frequently occurs in olefin caustic treatment. Using a SWS to process these effluents is poor technology selection and is strongly not advised. However, if this must be done, SWS units will experience red-oil fouling to a greater or lesser extent (Figure 8). Red-oil fouling varies in colour from yellow to orange to red and is a combination of aldol condensation, free radical polymerisation and Diels-Alder polymerization. Red fouling can be treated by neutralisation of the fouling precursors with scavengers or absorbing them from the solution using an aromatic solvent (Cuoq *et al.*, 2016).



**Figure 8** Red-Oil Polymer Beads Seen in Filtrate from Stripped Water

- 4) **Peroxides** can be formed from the oxidation of various fuel components. For benzyl, allyl and tertiary components this can occur at room temperature (Peyton, 2017). These species have been found where an MTBE unit is one of the sour water sources. They may also be present in chemical compounds being added to the system for treatment. Normally, if there is peroxide in the sour water it is the result of these chemical additions in the plant.

Peroxide can initiate a hydrocarbon polymerisation reaction and should be prevented from entering the sour water.

- 5) **Olefins**, particularly conjugated diolefins, may form polymers or gums in the presence of even trace quantities of oxygen. This is a common issue in water that has contacted coker naphtha or olefin-rich LPG streams as may be produced in a Fluid Catalytic Cracker Unit (FCCU) or associated downstream units.

- 6) **Thiophenes/thiophenols** are sulphur containing compounds that may be present in non-hydro-processed hydrocarbon fractions. In conjunction with oxygen and olefins these can form a gum-like substance (*Peyton, 2017*). This will be like the olefin polymer in Point 5 above, but have sulphur incorporated into its molecular structure.
- 7) **Phenols** are aromatic compounds with a hydroxide functional group formed by cracking processes in cokers and hydrocrackers. Phenols are generally soluble but can form insoluble crosslinked polyphenols in the presence of manganese or iron ions that are produced by the corrosion of steel (Orea et al., 2015). This phenomenon has been observed in heavy oil refineries in Canada and South America.

## Challenge 2: Treated Water Specification

Failure to meet stripped-water specification on ammonium or sulphur has the following potential causes:

- 1) Insufficient contact
- 2) Insufficient energy
- 3) Overloading
- 4) High acid-base bond strength
- 5) Ingress of sour water into the stripped water section

**Insufficient contact** is often a result of fouling or mechanical damage to the unit. Fouling has been discussed in the previous section. Mechanical damage to the column internals is generally the result of steam shock.

Liquid water expands by a factor of approximately 3000 when vaporized. Sudden vaporization or condensation can, respectively, create an enormous pressure surge or a vacuum. This can cause considerable damage to a column, as seen in Figure 9. This sort of incident almost always happens during startup or shutdown when sending cold liquid into a hot column or hot steam into a cold column. With the column normally isolated in these instances, there is no outlet for the sudden, large pressure change.



**Figure 9** Collapsed Internals in the Manway of a Column after Steam Shock During Start-up

Mechanical damage to the column internals could also be caused by vibration at the natural frequency of the trays or bed support plates. To avoid this, the spray-flow regime should be avoided, and column design guidelines adhered to.

**Insufficient energy** means simply not having enough steam or heat entering the column to meet specification. Often this is caused by fouling of the column reboiler and feed/effluent exchanger. The solution is to increase heat input and remove the fouling.

**Overloading** occurs when trying to push more feed through a sour water column than it can effectively handle due to hydraulic or heat exchanger limitations. This occurs if, when debottlenecking other sections of the plant or when there is a significant increase in the amount of nitrogen or sulphur in the crude slate, the capability of the SWS section is neglected.

**High acid-base bond strength:** Strong-acid anions (fluoride, chloride, bromide etc.) that are present will form an ionic bond with ammonium cations in the water that cannot be broken at the conditions of the SWS. The result will be failing to meet specification for ammonia in the treated water.

Conversely strong-base cations (sodium, potassium etc.) will form a bond with bisulfide anions ( $\text{HS}^-$ ) that will not break at SWS conditions. This may put the treated water out of specification for total sulphur.

The presence of strong ions can sometimes be due to inappropriate water being drained into the sour water sewer, e.g. fire water, spent caustic. These should be eliminated. Low levels of strong anions and cations will nevertheless often be present. If strong ions interfere with meeting the stripped-water specification, acid or base components can be injected to 'neutralize' these strong ions.

To adjust the pH of the sour feed water, caustic ( $\text{NaOH}$ ) is commonly used when a strong base is needed, while citric or acetic acid make good choices for acidifying requirements. Sulfuric acid is not recommended due to its potential to react with sulfide ions in the sour water and form elemental sulphur. Dosing rates can be based on: detailed analysis of the water, targeting a specific pH, or trial and error. When dosing acid or base into a SWS it is important not to overdose.

In one Asia-Pacific refinery the sour water contained 75mg/l of chloride and 120mg/l of sulphate. This resulted in 71mg/l of ammonia in the stripped water, which was higher than the required specification of 50mg/l. Total sulphur in the stripped water was less than 1mg/l. The addition of 100mg/l of sodium in the form of caustic reduced the ammonium level to 3mg/l still with less than 1mg/l of sulphur in the stripped water. Increasing the sodium dosage further to 1000mg/l resulted in less than 1mg/l of ammonium but the stripped water exceeded the specification for sulphur at 44mg/l, with the specification being 10mg/l. This was a result of the excess of the

strong-base sodium cations forming a strong ionic bond with bisulfide anions that then prevented them from being stripped from the water.

Depending on the configuration of the stripper, the injection point for the acid or base may also be optimized. For example, as the bisulfide is often more readily stripped than the ammonium it often makes sense to inject caustic a few trays from the bottom. This reduces the chance of the sodium binding to bisulphide and shortens the lag time between measurement (stripped water pH) and controller action (dosing rate), which can be significant. (*Weiland & Hatcher, 2012*)

**Ingress of sour water into the stripped water.** If the raw sour water leaks into the stripped water, the resulting mixture could be out of specification. The most likely location for a leak to occur is the feed/effluent exchanger.

### Challenge 3: Corrosion

The most common location for corrosion in a SWS system is in the overhead system, Figure 10. The condensing of acid gas results in reflux water with a very high concentration of ammonium bisulphide salts the overhead system, especially at lower temperatures.

Other corrosion mechanisms that have been observed or reported include:

- Hydrogen cyanide and free cyanide ions in the water
- Under-deposit corrosion
- Under-stripping
- Organic acid accumulation in the reboiler and lower stripper
- Erosion
- Titanium hydriding
- Ammonium Carbamate, caustic embrittlement, chloride pitting

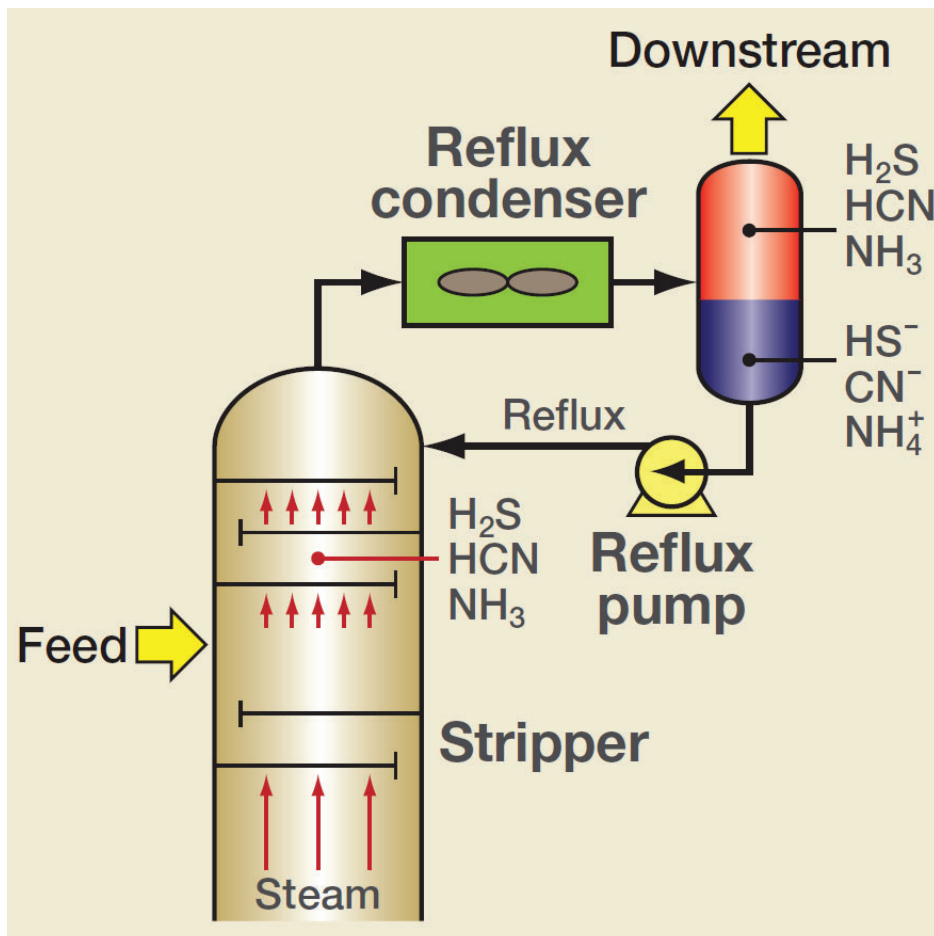


Figure 10 Reflux Overhead System of a Sour Water Stripper (Ie Grange, 2019)

**Ammonium Bisulphide ( $\text{NH}_4\text{HS}$ )** is present at percentage levels in the top sections of almost all refinery sour water stripper systems. While a reflux configuration typically results in a higher

concentration of  $\text{NH}_4\text{HS}$ , pump-around configurations are by no means immune to this sort of corrosion. Corrosion in these sections may be severe, as illustrated in Figures 11 and 12. The exact combination of conditions at which  $\text{NH}_4\text{HS}$  corrosion occurs is a complex function of wall shear stress (velocity), temperature,  $\text{NH}_4\text{HS}$  concentration,  $\text{H}_2\text{S}$  partial pressure and  $\text{NH}_3$  partial pressure (*Horvath et al., 2007*). It is important to note that almost all grades of carbon and stainless steel will corrode above 35wt%  $\text{NH}_4\text{HS}$ , even at very low velocities and temperatures (*Damin and McCoy, 1978*).



**Figure 11** Corroded Reflux Trays #2&#3 (top) and Sour Water Feed Tray #4 (bottom)



Figure 12 Corroded Stainless-Steel Pump Impeller from a Pump-around Loop

While this issue should be prevented in the design phase and any subsequent column re-ratings, it frequently is not. If this corrosion mechanism occurs the following steps can be taken to mitigate it:

- 1) Limit  $\text{NH}_4\text{HS}$  content in the overhead section by raising operating temperatures OR diluting the reflux with a stripped water recycle into the reflux/pump-around line. The maximum  $\text{NH}_4\text{HS}$  should not exceed 25wt% for carbon and stainless steels.
- 2) Increase pipe sizes to reduce velocities.  $\text{NH}_4\text{HS}$  corrosion rates have been shown to increase with higher velocity (*Scherrer et al., 1980*).
- 3) Free cyanide in the overhead can exacerbate this type of corrosion by chelating the iron sulphide layers on piping and vessel internals (*API 571, 2003*). Polysulphide dosing can neutralise free cyanides.

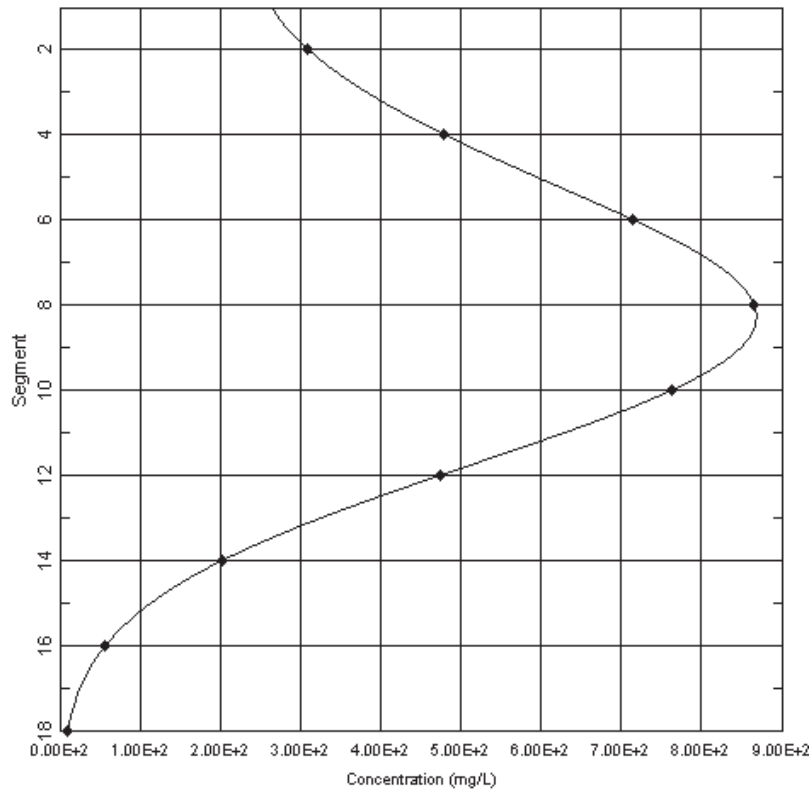
**Hydrogen Cyanide (HCN)** dissociates to free cyanide ( $\text{CN}^-$ ) with increasing pH. While HCN is quite soluble in water at ambient conditions, it becomes less so with increasing temperature and decreasing salinity. According to the International Cyanide Management Code (<http://www.cyanidecode.org/>): “At a pH of 11, over 99% of the cyanide remains in solution as  $\text{CN}^-$ , while at pH 7, over 99% of the cyanide will exist as HCN”

Cyanide has been implicated in several corrosion mechanisms:

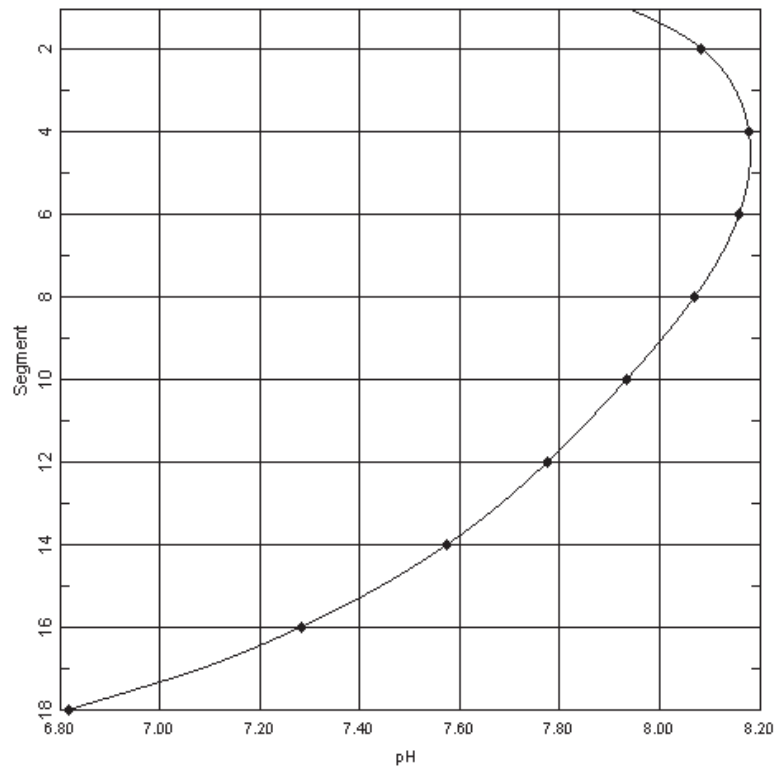
- 1) Aqueous-phase HCN greatly increases hydrogen permeation in sour waters. HCN is a known recombination poison which means that it retards the recombination of atomic hydrogen into molecular hydrogen (*NACE, 2006*). This can accelerate and promote hydrogen blistering of vessels and pipes.
- 2) API 531 (*API 571, 2003*) states that water at a pH above 7.6 with some dissolved H<sub>2</sub>S and 20ppmw HCN is known to be a blistering condition that promotes wet H<sub>2</sub>S cracking.
- 3) Cyanide has been shown to similarly promote carbonate stress corrosion cracking in alkaline sour waters with appreciable carbonate levels (*API 571, 2003*).
- 4) Cyanide is a complexing agent used industrially to extract minerals from ore and can form a large number of metal complexes of which ammonium ferricyanide and ammonium ferrocyanide are considered to probably occur in sour water strippers; both are highly soluble i.e. will dissolve the iron sulphide film coating the equipment that would otherwise possibly protect the equipment from further corrosion. (*NACE, 2006*).

In a SWS column, the H<sub>2</sub>S strips more readily than the NH<sub>3</sub>, thus typically pH initially increases as the water flows down the column before starting to decrease. There is also a temperature effect on both the solubility and pH. These competing effects result in there being a free cyanide concentration “bulge” midway through the column, as reported by *Weiland et al., 2014*.

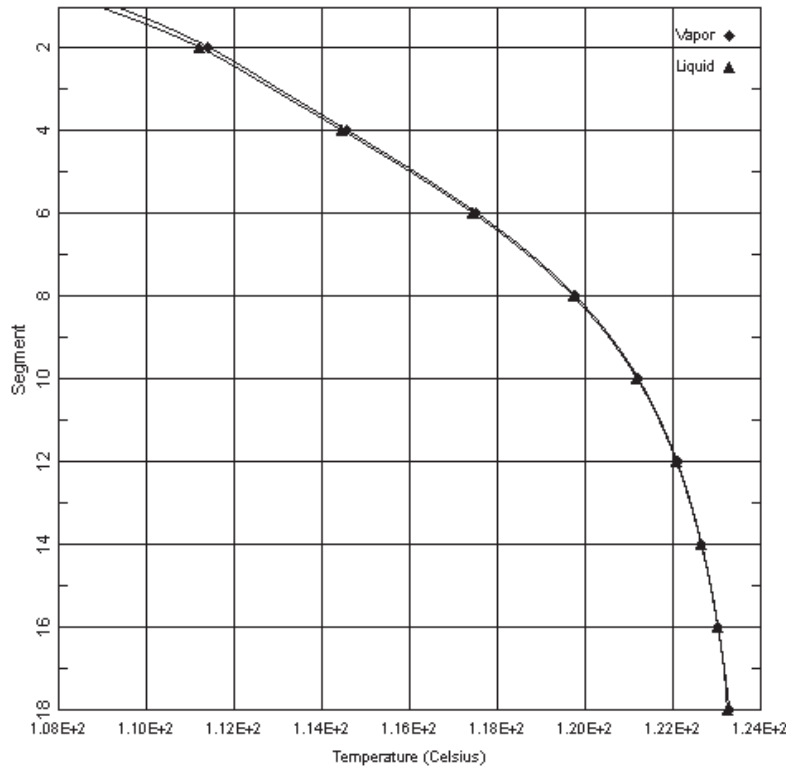
Profiles of HCN in the liquid phase, temperature and pH are shown in Figures 13 to 15 (where segment 1 is the top tray) from a process simulation. In this instance, an 18-trayed sour water column with direct injection, no reflux trays (reflux re-enters the column with the feed) and 75mg/l of HCN in the feed was simulated based on field testing results. A bulge in the cyanide concentration was predicted mid column at approximately ~850mg/l. This SWS unit had experienced hydrogen blistering in some locations but not the stripper column. While this phenomenon is possible, it would be best to have it confirmed on a test column, with analyses of samples collected from multiple stages to compare against the predicted profile.



**Figure 13 Free Cyanide in the liquid phase in a SWS**



**Figure 14 SWS pH profile**



**Figure 15 SWS temperature profile**

Free cyanide can be neutralized by the addition of ammonium or sodium polysulphide.

**Under-deposit corrosion** occurs because of scale (see fouling section) deposition. The scale has a different electro-potential to the metal onto which it deposits. There is thus a potential difference between the scale and the metal. These materials are in a conductive aqueous salt solution and a galvanic cell forms, thereby corroding the metal.

**Under-stripping corrosion** occurs when there is excessive amount of gas being stripped from the water (>5%) in the reboiler rather than in the stripper column itself. This may result in pitting corrosion in the reboiler (especially if there is a significant amount of CO<sub>2</sub> in the sour water). This type of corrosion is potentially initiated by the bursting of some of the large number of gas bubbles in the reboiler and lower part of the stripper column. In some cases, leaving an 'X' or 'V' pattern free of tubes in the tube sheet has assisted in degassing. This type of corrosion is more typical of amine units than sour water strippers and can be avoided by ensuring adequate stripping of the water in the stripper column rather than in the reboiler.

**Organic acid accumulation in the reboiler and lower stripper.** It is possible for some volatile organic acids to be stripped into the vapour phase in the stripper column and reboiler and later condense higher in the stripper column where the temperatures are lower. They thus become "trapped" in a loop inside the SWS unit. An example of this is shown in Figure 16 where acid has condensed on two cold spots where the platform above was joined to the reboiler vessels shell.



Figure 16 Two 3mm Grooves in Reboiler Shell near the Vapour Outlet (pH of 6)

Cold spots should be avoided on the reboiler shell and lower part of the stripper column. Good insulation should be maintained over the complete column and cold spots (e.g. welding ladders to column and reboiler shells) should be minimized as far as practicably possible. Organic acids should also be minimized in the feed if possible.

**Erosion** occurs where solid particulates or water droplets collide with excessive force against the metal of the vessel walls, pipe bends, pump impellers, etc. The following considerations will help avoid erosion:

- Reduce liquid velocities
- Use long-radius elbows (if corrosion found on elbows)
- Filter the inlet sour water if it contains appreciable solids
- Eliminate other sources of corrosion in the system that may be generating particulates
- Install impingement or sacrificial plates in areas where there is a high-velocity flow of water into a gas space, e.g. the return into the column from a thermosyphon reboiler.
- Remove areas of high localized velocity from the design by choosing appropriate vessel internals

**Titanium Hydriding** results from the absorption of atomic hydrogen by titanium. Titanium is sometimes used in SWS condensers (Hopkinson and Fermin Hernandez, 1988). This reduces the ductility of the steel and makes it brittle and vulnerable to fracturing/damage should mechanical forces been exerted on the condenser.

When titanium is in contact with aluminum, carbon steel, or stainless steel it forms a galvanic cell releasing hydrogen, this will hydride the titanium. Such couples can also form due to corrosion of lower alloys upstream of or in contact with the titanium components. Anodizing the titanium provides it with greater resistance to hydriding.

**Ammonium Carbamate, caustic embrittlement, chloride pitting and many others.** There are a variety of other corrosion mechanisms cited in the literature relating to SWS systems. These corrosion mechanisms are not commonly encountered. In general, once the mechanism has been identified, eliminating or neutralizing the component that has caused the corrosion in conjunction with optimizing local conditions is normally sufficient to resolve the issue.

#### Challenge 4: Off-Gas Hydrocarbon Content

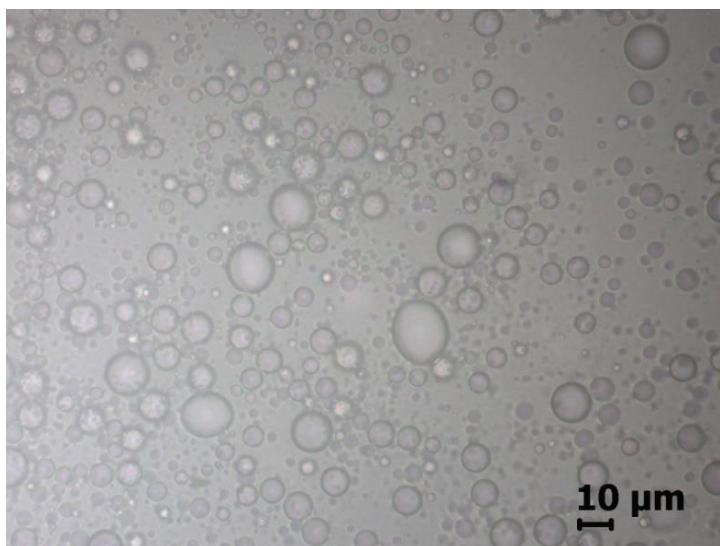
Hydrocarbons that enter the SWS will mostly be stripped and sent with the overhead gas to a Sulphur Recovery Unit (SRU). This may create operational problems for the SRU and be detrimental to its performance. Even a small increase in heavier hydrocarbons can result in a large increase in the amount of air required for combustion in the SRU reaction furnace, a phenomenon that is aggravated when the hydrocarbon content of the water is not stable. The following may occur in the SRU because of hydrocarbons in the sour water:

- Decreased hydraulic capacity
- Unstable plant operation due to variable air demand
- Damage to the SRU reaction furnace caused by rapid temperature variations
- Reduced efficiency due to poor H<sub>2</sub>S to SO<sub>2</sub> ratio control
- Reduced efficiency due to increased CS<sub>2</sub> formation
- Increased operating pressure from catalyst bed plugging by soot deposition from incomplete hydrocarbon combustion
- Reduced catalyst activity by catalyst blockage from aromatic cracking
- Reduced sulphur quality due to soot in the sulphur product, resulting in 'black sulphur'
- Soot fouling of the sulphur plant waste heat boiler and condenser

These effects are extensively documented in the paper by *Klint 2012*.

Hydrocarbons in water streams can be present in three forms (*Sheilan et al., 2014*):

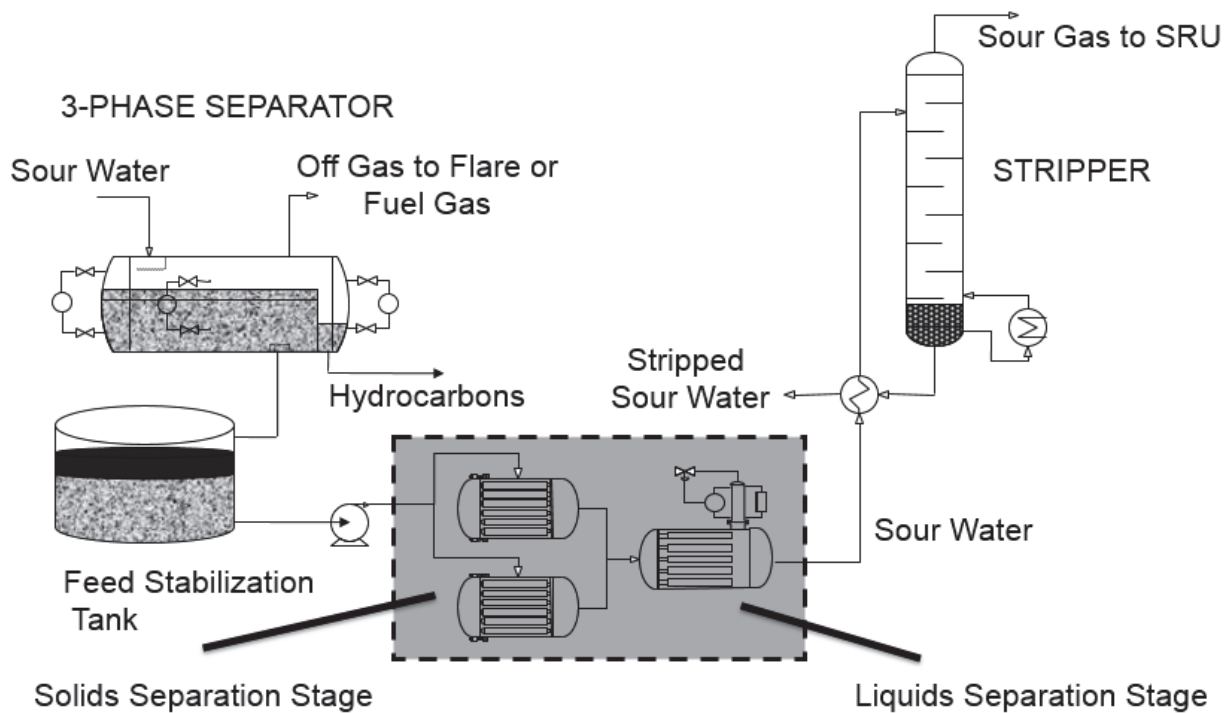
- 1) **Dissolved hydrocarbons.** All hydrocarbons have a degree of solubility in an aqueous phase. The extent of hydrocarbon solubility in water will depend on the pressure, pH, temperature and hydrocarbon type. It is impossible to observe dissolved hydrocarbons in a water phase as it is indistinguishable from pure water. In general, the solubility of hydrocarbons in water can range from a few ppmw to a few hundred ppmw.
- 2) **Free hydrocarbons.** These will not interact with the bulk water and will generally separate within a few minutes. Free hydrocarbons will form into a layer above or below the water phase (depending on the relative densities). The quantity of free hydrocarbons can vary from 100 ppmw to percentage levels.
- 3) **Emulsified hydrocarbon.** Under normal conditions, hydrocarbons will be either free or dissolved in a water phase. However, under certain conditions, hydrocarbons can form very small droplets in the water phase (see Figure 17). These droplets are stabilized by molecular surfactants (as created by soaps or detergents) and by small-sized suspended solids. Emulsion droplet sizes can range from a few microns to about 500 microns. Micro-emulsions, which are the most stable emulsion type (and can take weeks to naturally separate) are typically found when droplet sizes are less than 10 microns.



**Figure 17 Oil Micro-emulsion in Water**

In general, everything lighter than the diesel fraction will be removed in a conventional single-column stripper. Hydrocarbons also pose a fouling risk and should be eliminated from the SWS feed. Minimization of hydrocarbons from the sour water feed may be achieved by:

- Removing free hydrocarbons in the inlet three-phase separator. In general, 25min of residence with a liquid level at 50 to 60% of drum height is optimal.
- Installing a sufficiently large feed stabilization tank with hydrocarbon skimming facilities. Sometimes these tanks have several days of residence time during which time some emulsified hydrocarbon will come out of emulsion and may be removed.
- Installing a coalescer (typically these require pre-filters; see Figure 18) to remove emulsified hydrocarbons.
- Using a hydro-cyclone separator to reject a hydrocarbon-rich light phase back to the feed stabilization tank.



**Figure 18 Optimal Filtration and Coalescing Scheme (Sheilan et al., 2014)**

In some plants, the flash gas from the sour water inlet flash drum/three phase separator is fed directly into the sour water stripper off-gas. This is not a good design practice and can often be a large source of hydrocarbon supply to the SRU. Typical alternatives for this gas are recovery to the light-ends section of the refinery or directing the stream to a flare or thermal oxidizer where regulations allow. In cases where no condensable hydrocarbons are expected, this gas stream may be directed to the quench column of an amine-based Tail Gas Treating Unit (TGTU).

## Challenge 5: Feed-Water Quality Management

Refinery water systems are often neglected and poorly understood. The key to good water management is having a good understanding of the plant's wash water needs, the expected ammonium bisulphide concentrations of waste waters, and the contaminants in the various source and product streams within the sour water collection and processing units based on regular and detailed water analysis. A good strategy uses this knowledge to optimize water reuse, concentrations and circulation, and to minimize reprocessing and waste. This is a non-trivial task as there are many aspects that need to be considered, some of which are described below.

**Saltwater** - In many plants brine or surface water is used for firefighting, cleaning of equipment, etc. This is often seawater or well water that contains a large amount of salt. These waters should not be allowed to enter the sour water sewer as they may make it difficult to meet the treated water specification from the SWS unit.

**Spent Caustic** from LPG treating is often disposed of in the sour water stripper system. To prevent the unit from going off-specification with respect to  $H_2S$ , acid dosing is required to neutralize the sodium content. Control of the acid dosing rate can be extremely challenging as the spent caustic is batch-dumped into the system and can often vary significantly in composition from one batch of spent caustic to the next. Caustic dumping is not a recommended practice, however, when there is no alternative it is recommended that the spent caustic be put into a storage tank with reasonable residence time and slowly fed into the SWS feed at low quantities. In this way the delivery rate of the caustic to the SWS unit can then be controlled and the pH of the blended sour feed water effectively managed by acid dosing.

It is not advised to send spent caustic from MEROX units into the SWS system. These caustics contain potentially fouling disulphide oils and chrome-based MEROX catalyst which can turn the stripped water a startling blue and create operational difficulties for the downstream waste water treatment plant.

**Phenol** in the sour water will largely not be removed in a SWS unit (*Weiland & Hatcher, 2013*) and will pass through to the treated water. Phenolic water cannot be processed in most conventional wastewater treatment facilities. The most common method for dealing with this is to send the phenolic water to the crude oil desalter at the refinery inlet for back-extraction. Other treatments using light, chemical dosing, absorption, membrane separation and ion exchange exist to treat phenol content but are typically expensive.

For phenolic back-extraction into the crude oil to work, it is important to segregate the phenolic and non-phenolic water sources in the refinery. It is also important to ensure that minimal caustic enters the phenolic water system as sodium in the desalter wash water will decrease desalter desalting which can have a large adverse effect on refinery economics (shorter intervals between

decoking on the thermal cracking units and potentially a large increased in FCCU catalyst consumption).

**Selenium** is isomorphous with sulphur and typically the more sulphur in a crude the more selenium is also present in it. Almost all selenium entering the refinery will leave with the stripped water from the SWS unit as hydrogen selenide and selenocyanate, as opposed to selenite or selenate, being reported as the predominant form of selenium ion in refinery waste water (*NAMC, 2010*). This problem will need to be managed downstream of the SWS unit prior to the water's release due to the aquatic toxicity of this element.

**Cascading wash waters** with low levels of contamination or low concentrations of ammonia and hydrogen sulphide to serve as wash water on other units can reduce the volume of sour water generated on a refinery and increase the energy efficiency and conserve capacity of the sour water stripper unit, with proportionally more energy being used to strip the water and less being used for latent heating and cooling. Always be aware of maximum concentration limits prescribed for the SWS unit when increasing the ammonium bisulphide content.

**Bypass** water streams that do not need treatment around the sour water stripper unit. Typically, mildly contaminated water streams that contain less than 50ppm of ammonium and less than 10ppm do not need to be stripped, depending on local legislation and the extent to which these streams may be diluted.

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### **Biography - Philip le Grange - Senior Treating Engineer**



Working for *Sulphur Experts*, Philip has performed troubleshooting, optimizing, commissioning and training on the amine and sour water systems at 70 sites across 29 countries. He has been in the oil and gas industry for 15 years and prior to consulting has worked in both Operating Engineer and Plant Designer roles.

He has an excellent track record at resolving operational challenges and has authored papers and articles for *Industrial & Engineering Chemistry Research*, *Laurence Reid Conference*, *GPA Conferences*, *Hydrocarbon Engineering*, *TCE Magazine*, *PTQ* and *Sulphur Magazine*. Further, he is one of the primary authors and editors of the textbook *Amine Treating and Sour Water Stripping* published by *Sulphur Experts*



## **Appendix I**

### **Reducing Hydrocarbons in Sour Water Stripper Acid Gas**

# Reducing Hydrocarbons in Sour Water Stripper Acid Gas

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## **Abstract**

All refineries and some gas plants must process their waste water. Sour Water Stripping is the first step in the wastewater treatment process. In this process all acid or odiferous components are removed from the water. Whatever is removed is typically sent to the sulphur plant for further processing.

Typical sour water acid gas (SWAG) is composed only of  $H_2S$ ,  $NH_3$  and water. However, hydrocarbons are often present in the sour water feeding the stripper, and they are stripped out and sent to the sulphur plant with the SWAG. Hydrocarbons can create a number of operational and performance problems in the SRU and need to be eliminated.

This paper discusses how to minimize the level of hydrocarbons in sour water, and thereby protect and maximize the efficiency of the sulphur plant.

Several strategies will be outlined which can be implemented by refiners either in part or as a whole to mitigate hydrocarbon contamination of the SWAG. These strategies will range from reducing hydrocarbons in the individual water feeds, to optimization of the flash and holding tanks, to adding emulsifying agents to the holding tank or utilizing hydrocarbon separation technology on the water feeding the stripper itself.

The paper will additionally identify the problems immediately resulting from this hydrocarbon contamination of the SWAG routed to the SRU and its effect on the plant operation and efficiency

## INTRODUCTION

“Sour Water Stripping” (SWS) is one of the first stages in the waste water treatment process in many industrial operations, and especially in refineries. Water streams from throughout a refinery are typically sent to the stripper, which is designed to remove both H<sub>2</sub>S and ammonia from the water. There are several designs of sour water strippers, all playing upon the same theme of using heat to break the bond between NH<sub>4</sub>SH in the wastewater. This liberates gaseous ammonia and hydrogen sulphide in a produced acid gas. In some cases the ammonia and H<sub>2</sub>S are separated and sent to individual destinations, but in the majority of SWS set-ups the effluent acid gas from a sour water stripper overhead is processed in the sulphur plant (SRU).

Hydrocarbons may also be present in the water feeding the stripper. If and when this occurs, most hydrocarbons will be vaporized and flow with the acid gas. This creates problems in the Sulphur Recovery Unit (SRU), both operationally and mechanically. In Sulphur Experts' experience, SWS Acid Gas containing more than 2 percent hydrocarbon is a firm indication of problems upstream of the stripper.

This paper discusses how to mitigate the presence of hydrocarbons in sour water feeds, thus reducing fouling, corrosion and many associated operating problems both in the SWS and the SRU.

## SOUR WATER STRIPPING PROCESS

The purpose of a sour water stripper is to remove components that are toxic or cause undesired odour; primarily H<sub>2</sub>S and NH<sub>3</sub> (ammonia) as well as dissolved gasses, solids and hydrocarbons.

The process involves flowing the water down a tall stripper tower (equipped with either trayed or packed internals) being contacted counter-currently with steam. When sour water first enters the stripper, H<sub>2</sub>S and NH<sub>3</sub> is dissolved in the water as a salt (NH<sub>4</sub>HS) and cannot be removed as the salt has no vapour pressure. By heating the sour water, the dissolved H<sub>2</sub>S and NH<sub>3</sub> will phase transfer into their vapour forms, which can then be stripped. Any other volatile species are also liberated.



There are many wastewater sources in a refinery, all of which have different contaminant compositions, flow rates and pressures. In addition, some sources may be continuous while others are intermittent. As a result, without proper upstream equipment, design, and operation, the chemical composition and flow of water to the SWS may vary significantly. This can result in many operational difficulties both for the stripper and the downstream sulphur plant, the destination for the gasses stripped from the water.

The most common sources are: atmospheric crude columns, vacuum crude towers, steam crackers, fluid catalytic cracking (FCC), hydro-desulphurization (HDS) units, catalytic hydrocracking (ARDS) units, coker units, amine reflux, and TGTU quench towers.

H<sub>2</sub>S and NH<sub>3</sub> concentrations are the highest in water from the HDS, ARDS, and FCC units. Any water stream containing 10ppm or more of H<sub>2</sub>S should be routed to the SWS.

Proper removal of contamination from the sour water is extremely important for the next steps in wastewater treatment; often a biological treater which cannot survive under high hydrogen sulphide levels.

## HYDROCARBONS IN SOUR WATER

Hydrocarbons in water streams can be present essentially in three forms:

- 1) **Free hydrocarbons.** These will not interact with the bulk water and will tend to separate within a few minutes. Free hydrocarbons are normally observed by the formation of a top hydrocarbon layer above the water phase (or below depending on the density difference). The levels of free hydrocarbons can vary from hundreds of ppm to % levels.
- 2) **Soluble Hydrocarbons.** All hydrocarbons will have certain solubility (called miscibility) in water phases. The extent of hydrocarbon solubility in water will depend on the pH of the water, water pressure and temperature and the type of hydrocarbon. It is impossible to observe dissolved hydrocarbons in a water phase as it is indistinguishable from pure water. In general the solubility of hydrocarbons in water can range from few ppm to a few hundred ppm.
- 3) **Emulsified hydrocarbon.** Under normal conditions, hydrocarbons will be either free or dissolved in a water phase. However, when conditions are right (including the presence of surfactants and energy), the hydrocarbon contaminants can form very small droplets in the water phase (Figure 1). These droplets are stabilized by molecular surfactants (similar to soaps or detergents) and also by small size suspended solids. Emulsion droplet sizes can range from a few microns to about 500 microns. Micro-emulsions, which are the most stable emulsions available (and can take weeks to separate) are typically found when droplet sizes are below 10 microns.

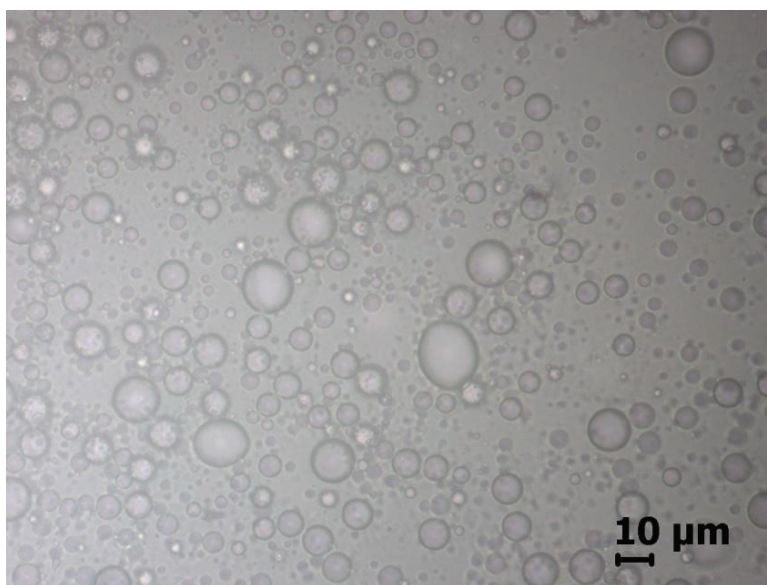


Figure 1 Microphotograph of a water and oil micro-emulsion.

## SOUR WATER SOURCES

In a refinery setting or any plant in general, sour water can be generated in many locations. Water for process applications is used in many ways such as: quench water, steam, wash water and is also generated by the various distillation fractions where water is co-distilled with certain hydrocarbons. Figure 2 shows the diversity of a number of sour waters originating from various units.



**Figure 2**      **Various water streams feeding SWS systems**

Primary sour water sources include:

- Atmospheric and vacuum crude towers: water is produced by condensing overhead steam streams. Vacuum towers may also contribute sour water from ejectors and barometric condensers.
- Thermal and catalytic cracking units: steam condensate from injection, stripping and aeration. The heavier or more viscous the feed, which contain sulphur, produce  $H_2S$  when hydrogenated. Ammonia is also produced from hydrogenation of organic nitrogen compounds.
- Hydrotreater and hydrocracker wash water from high and low pressure separators
- Cokers – delayed and fluid types plants. Water is produced from decoking and quench water
- Flare seals and knock out drums
- Hot condensates from throughout the refinery which may have had contact with hydrocarbons (often the concentration of contaminants in these streams is low)
- Any refinery water draw boot: each contains a different sour water composition and flow, depending on crude type and the severity of the process. Manual level controls can also affect the hydrocarbon content of the water especially if they are accidentally left open for too long.

There are various analytical methods available used to test water samples for hydrocarbon-like substances. The most common are:

- Proton Nuclear Magnetic Resonance ( $^1\text{H}$ NMR). It will detect hydrogen atoms attached to carbon atoms in hydrocarbon structures. The technique uses the signals from electrons in the hydrogen atom and these how interact with the neighboring carbon atoms and hydrogen atoms
- Infrared spectroscopy (IF or FTIR). This technique detects alkyl residues, olefin residues and aromatic residues by interaction of infrared energy light with the molecular component. FTIR are IR systems with special mathematical result treatment using a curve fitting technique called Fourier Transformed.
- Gas Permeation Chromatography (GPC) is technique very similar to liquid chromatography. It uses a polymer to separate the various components in a mixture. The separation is obtained by “size exclusion”
- Gas Chromatography coupled with Mass Spectrometry (GC-MS) is capable of separating most components in a mixture provide exact molecular weight of each component.

The pH of the sour water has a direct relationship with the solubility of hydrocarbons in water; the higher the pH, the higher the solubility, as is shown in Figure 3.

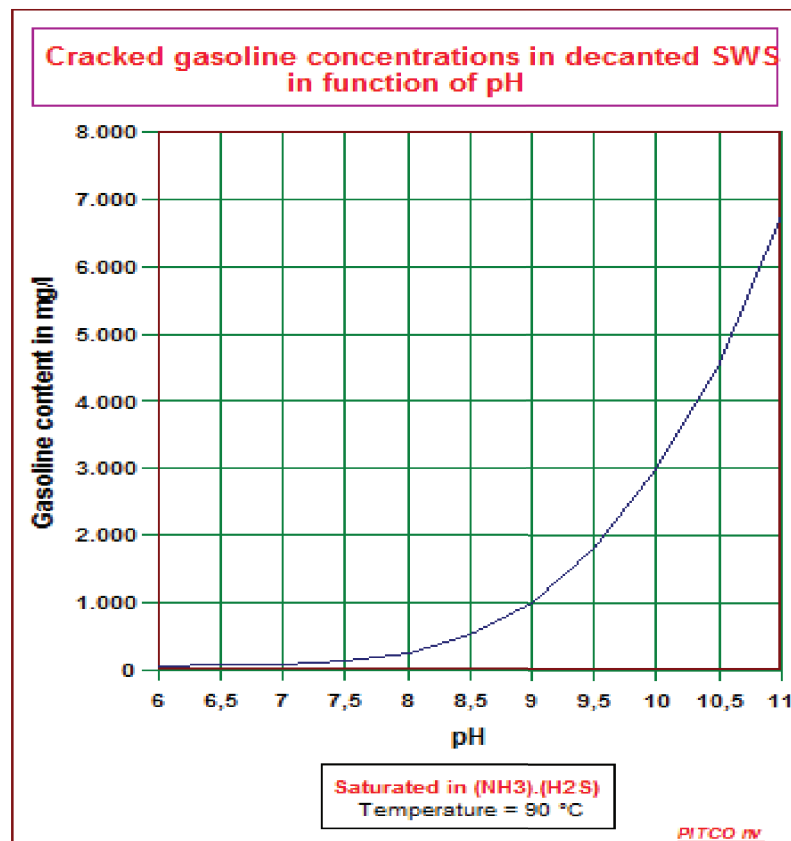


Figure-3 Relationship between pH and gasoline solubility in sour water

## Sour Water Process Description

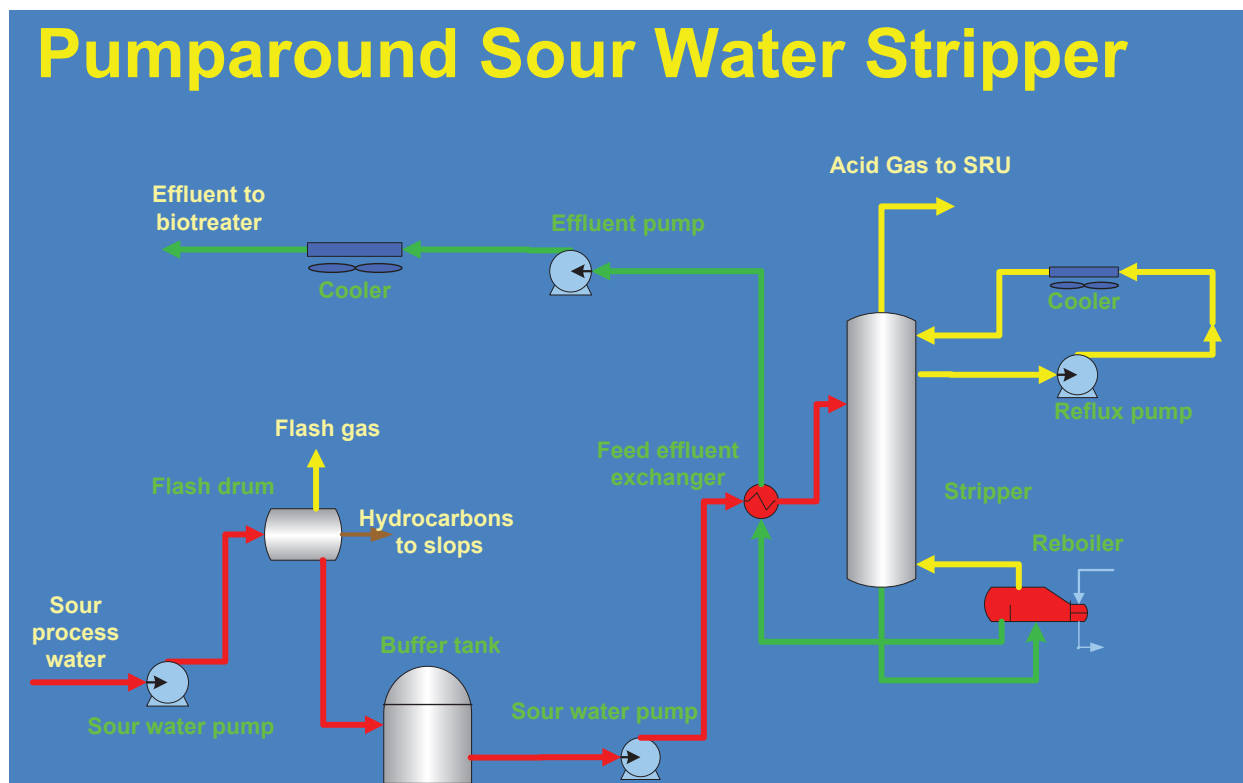


Figure-4 A generalized sour water process description is summarized below:

1. Various sour water streams are collected from throughout the refinery and sent to the flash tank. Flash tanks remove entrained gasses and condensable liquid hydrocarbons by allowing the water to de-pressure and settle for at least 5 minutes.
2. The degassed water flows to a holding, or settling tank. In this tank there may be further degassing as well as the separation of liquid hydrocarbons and oil which float to the surface of the water. If the residence time is high enough, the composition of the water stabilizes and allows for a consistent flow and composition of water to the stripper.
3. Exiting the settling tank, the water is heated in a heat exchanger ("feed/effluent exchanger") by hot, stripped water which is exiting the stripper.
4. The heated sour water is injected near the top of the stripper tower, where it falls and is stripped of  $\text{H}_2\text{S}$ ,  $\text{NH}_3$  and any remaining hydrocarbons, by the steam rising from the bottom. Steam is typically produced in a reboiler but may also be introduced directly as live steam.
5. The overhead of the stripper is normally a pump-around cooling section which cools the steam to  $85^\circ\text{C}/185^\circ\text{F}$ , the proper temperature for sending SWAG to the SRU. Alternatively, a reflux system may also be used for the same purpose. These systems recover a portion of the water in the overhead stream, minimizing the amount being sent to the SRU.
6. The stripped water is cooled in the feed/effluent exchanger then pumped to various areas for further processing (crude unit desalter, biological treatment, etc.).

## EFFECTS OF HYDROCARBONS ON THE SULPHUR PLANT

Preventing hydrocarbons from entering the sour water stripper will in turn prevent hydrocarbon rich acid gas from entering the sulphur plant (SRU). There are several reasons why it is advantageous to minimize hydrocarbon in the SRU feed, the most important involving:

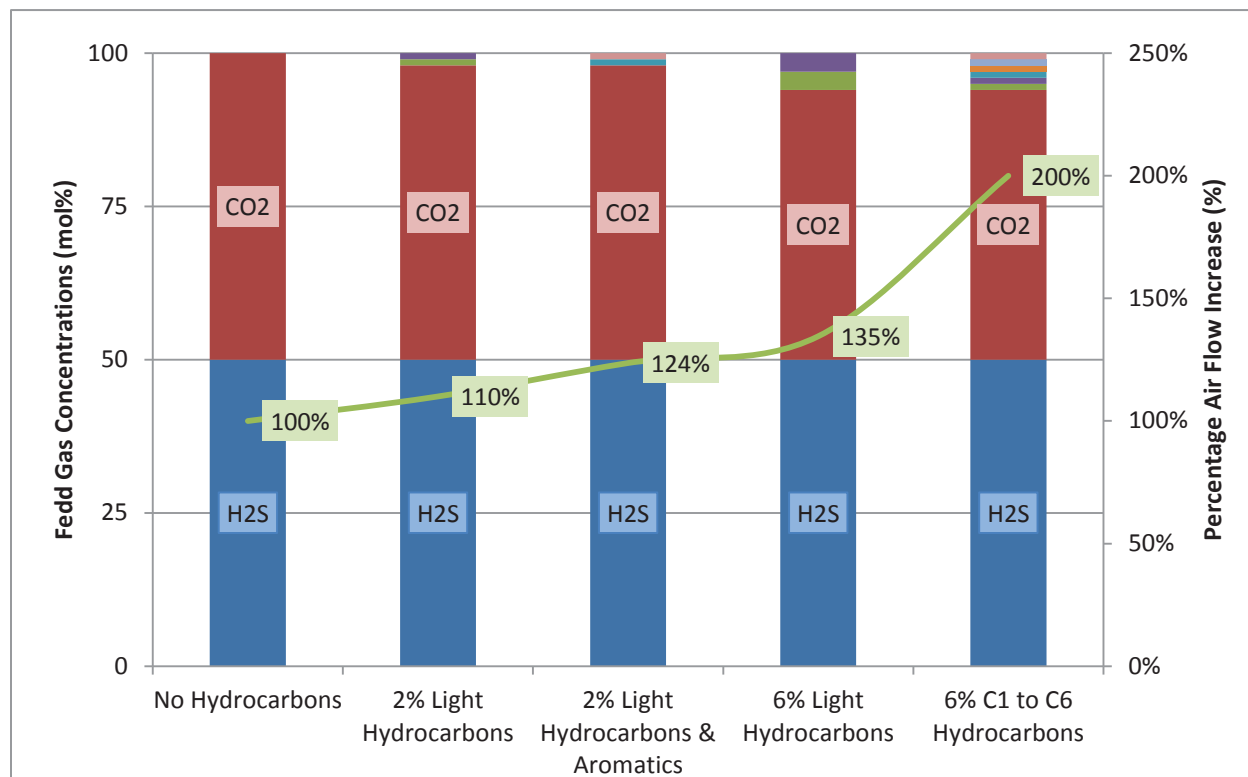
- Difficulties maintaining stable operation;
- Decreased capacity;
- Lower efficiencies; and
- Potential issues with catalyst deactivation and sulphur quality due to soot.

Sulphur plants require combustion air in the main reaction furnace to oxidise part of the  $\text{H}_2\text{S}$  contained in the feed gas to form  $\text{SO}_2$  prior to entering the downstream catalytic stages of the modified-Claus process. The modified-Claus process is a reversible reaction and its success is highly dependent on reacting two moles of  $\text{H}_2\text{S}$  with one mole of  $\text{SO}_2$  to form sulphur and water. Having either too much  $\text{H}_2\text{S}$  or too much  $\text{SO}_2$  will limit the equilibrium conversion of the catalytic stages and impact the overall sulphur recovery efficiency of the SRU.

As previously mentioned,  $\text{SO}_2$  is formed in the reaction furnace by the combustion of air and  $\text{H}_2\text{S}$ . However, since some  $\text{H}_2\text{S}$  is still needed for the downstream reactions, the air flow rate to the reaction furnace is controlled such that only *a portion* of the  $\text{H}_2\text{S}$  is combusted to  $\text{SO}_2$ , resulting in a sulphur plant furnace that operates in a significantly reducing environment; this makes the air flow to the furnace a critical limiting control parameter.

In order to control the air flow, most sulphur plants use a fixed air-to-feed gas flow (or mass) ratio which controls the majority of the air flow rate to the SRU and is dependent on the feed gas flow rate. This is however, a very basic type of flow control, and on its own is not enough to ensure maximum performance from the Claus plant. In order to maintain a proper  $\text{H}_2\text{S}/\text{SO}_2$  ratio in the Claus tail gas, an analyser is used to measure the  $\text{H}_2\text{S}$  and  $\text{SO}_2$  concentrations at the tail gas location and force fine-tuning of the air flow rate to the reaction furnace. Unfortunately, due to the location of this analyser at the back end of the process, a certain amount of lag time is inherent in the control system. Since a small amount of hydrocarbons consume a large amount of oxygen in the reaction furnace, this directly impacts the formation of  $\text{SO}_2$  by potentially limiting the available  $\text{O}_2$  and if these changes in composition occur quickly and rapidly, then this can result in significant operating problems for the SRU. Ideally, air flow should be controlled within  $\pm 0.5\%$  of that necessary to maintain a 2:1  $\text{H}_2\text{S}$ -to- $\text{SO}_2$  ratio in the Claus tail gas. Small changes in the hydrocarbon composition of the SWS system can result in the inability of a plant to maintain proper air flow control, resulting in significant efficiency loss.

As the concentration of hydrocarbons increases, so does the amount of air required to combust them. The heavier the hydrocarbon, the more air required. Therefore, even very small amounts of heavy hydrocarbons ( $\text{C}_6+$ ) can result in a significant air demand. Most sulphur plants are limited by their air blowers to deliver sufficient air, therefore adding anything to this process that competes for oxygen will limit the amount of sulphur that can be processed in an SRU. Figure 5 illustrates the impact than an addition of hydrocarbons to a simple acid gas, and the effect on air flow rate.



**Figure 5 - Air Flow Requirement for Various Feed Gases**

As seen in Figure 5, the air flow rate for a simple acid gas increases by 10% with the addition of 2% light hydrocarbons ( $C_1$  and  $C_2$ ), and adding increasingly more and heavier hydrocarbons (i.e., equal amounts of  $C_1 - C_6$ ) can double the air required to combust them. This increase in the air requirement will reduce the processing capacity of a sulphur plant.

In addition, to a point, hydrocarbons in the feed gas will increase the formation of  $CS_2$  in the reaction furnace and decrease the partial pressure of  $H_2S$  and  $SO_2$  in the system. This will reduce the equilibrium conversion rates of  $H_2S$  and  $SO_2$  in the catalyst beds, thus reducing the overall efficiency. In addition, the higher COS and  $CS_2$  formation in the reaction furnace also requires higher first converter operating temperatures and/or the use of specialised catalyst to convert these compounds back to  $H_2S$ . They otherwise contribute to significant efficiency losses in a sulphur plant, which has an impact on operating costs and equipment sizing.

Proper mixing of the feed gases and air, as well as adequate residence time are required in the reaction furnace in order to ensure full combustion of hydrocarbons contained in the feed gases, often requiring the installation of specialised burners and a minimum operating temperature of  $1050^\circ\text{C}$  ( $1920^\circ\text{F}$ ). If not properly mixed, hydrocarbons contained in the feed gases can form soot or may not be fully combusted. Soot deposition can plug the active sites on Claus catalyst beds and may result in high pressure drops through the unit, thus resulting in lower processing capabilities of the SRU and discolouration of the sulphur product, resulting in a grey sulphur product. Non-combusted aromatic hydrocarbons, particularly toluene and xylenes, can rapidly deactivate standard alumina catalyst requiring frequent shutdowns to replace catalyst. Aromatic

hydrocarbons may also result in discolouration of the sulphur product, resulting in green or brown sulphur.

It is clear that there are many reasons to ensure that hydrocarbon content of feed gases being processed in a sulphur plant must be minimized in order to ensure good operability and reliability of a sulphur plant.

## **EFFECTS OF HYDROCARBONS (AND SUSPENDED SOLIDS) ON THE SOUR WATER STRIPPER**

Hydrocarbons in the sour water feeding the stripper can increase the risk of serious fouling in the stripper internals, reboiler and bottom section of the tower. Often the “black shoe polish”, which is found in sour water stripper bottoms, contains heavy hydrocarbons in the matrix.

Suspended solids in the sour water feed are fairly common, especially in plants associated with coker units. In addition, there is a tendency to add contamination from other sources into the sour water. To some extent these will settle in the upstream feed stabilization tanks however, a considerable portion will be contained in the water outlet. The effects of suspended solids can be somewhat similar to hydrocarbons, as they will cause deposition on metal surfaces leading to ineffective flows and under-deposit corrosion. The presence of hydrocarbons and suspended solids exacerbate the effect as the suspended solids will agglomerate with certain hydrocarbons generating a highly fouling material. This deposition can cause reduced stripping efficiency, corrosion and excessive maintenance costs.

The effluent (stripped) water can contain significant levels of suspended solids due to inlet contamination or corrosion of process internals. In many cases the water is sent to waste water plants where suspended solids will be detrimental to the water treatment process, and also increase the amount of sludge generated. Additionally, about 50 percent of refineries worldwide use stripped sour water as desalter wash water. The presence of solids will cause enhanced emulsification impacting the effectiveness of water and crude separation in the desalter unit. This can lead to increased salts in treated crude generating higher corrosion rates in the crude unit overhead. In fact, it is possible that many problems of crude unit corrosion, desalter upsets, desalter effluent quality and additive use is directly tied to suspended solids in SWS water outlet.

## **MINIMIZING CONTAMINATION IN THE SOUR WATER**

The best avenue to minimize hydrocarbons in sour water feeds is to ensure that the hydrocarbon is not in the water in the first place. This is carried out by a comprehensive and thorough evaluation of sour water generation points. In refineries the majority of these are Crude units, FCC units, Coker units, Hydrotreater/Hydrocracker units and visbreaker units. All these units will have overhead accumulators or other water/oil separators and flash tanks. Optimizing the equipment needed to enhance the water/hydrocarbon separation is the best option to remove these contaminants from the sour water. In some cases, simple instrumentation failures in these vessels can cause hydrocarbons in the sour water stream. Other avenues to minimize the hydrocarbon content of the sour water are:

- Optimizing the sour water flash tank operation. Sometimes design changes to the tank interior may be necessary to ensure minimal hydrocarbon breakthrough;

- Optimizing the sour water holding tank (also called feed stabilization tank). This is related to its use, maintenance and design;
- Utilizing filtration and/or coalescing technology on the sour water feeding the feed/effluent exchanger to remove suspended solids and recover hydrocarbons; and
- Optimizing the operation of the SWS.

## **Sour Water Flash Tank**

The flash tank is a three phase separator; its purpose is to separate water, oil and gas. This is achieved through pressure drop and residence time; the greater the pressure drop or greater the residence time, in theory, the greater the separation of the three phases.

Flash tank operation is therefore at its peak when the pressure in the vessel is as low as possible and residence time maximized. The minimum recommended residence time is 20 minutes. The lower the pressure, the more likely hydrocarbons will flash off, as pressure has a direct effect on the vaporization point of hydrocarbons. For example, Butene-1 has a pure boiling point of -6°C, at atmospheric pressure, but this increases to 50° C at 5 barg.

The pressure is set by the destination pressure of the flash gases. These gases are normally sent to flare, incineration, or a low pressure fuel gas amine absorber. No matter the destination, the flash tank should always be run at the lowest possible pressure; just enough to push the water and flash vapour to their next respective process. Under no circumstances should flash gas be routed to the SRU, as the flash gas composition will consist almost entirely of hydrocarbons, constantly fluctuating in both flow and concentration.

Residence time is a function of the size of the vessel, the level the water is maintained at, and the flow rate of water. The vessel size obviously is nothing the operator has any control over. The water level however, can be controlled, and should be maintained at 50-60 percent. This maximizes liquid residence time but still allows for vapour disengaging space. When hydrocarbons flash from liquid to gas they can expand by up to 300 percent, and if the tank was too full, water would be carried with the flash gas.

If the flash tank utilizes weirs, they will typically be set at a height of 50-60 percent. The water level should be maintained at 7-8 cm below the weir height, allowing liquid hydrocarbons to then flow over into the oil side of the weir. When both the size of the tank and liquid level are set, then the only option to reduce residence time is to reduce the water flow to the vessel. This can sometimes be accomplished by a detailed survey of all the various water streams feeding the sour water system – are they all necessary? If the water does not contain toxic or odorous contaminants, it does not need to enter the system. Such examples are fire or ballast water streams (these streams should never be introduced to sour process water feeds).

## **Sour Water Holding Tank**

Similar to the flash tank, this low pressure vessel should be operated at 50-60 percent full (or however much is possible, depending on the needed storage capacity). A large portion of the tank must be left empty to allow for upsets in the downstream stripper that may necessitate the need for water to be stored for several hours (or sometimes days). The longer the residence time, the better hydrocarbon separation will be. As well, the higher the chance that the mixing of all the water streams will be complete and the composition of the water feeding the stripper will be consistent.

Along with liquid height control, the location of the feed and discharge of the water lines will also play a large role in residence time. The inlet and outlet nozzles should be located at opposite ends of the vessel. The outlet nozzle is often 600 mm off the bottom of the tank so that precipitated solids or heavy oils that sink do not get sucked along with the sour water.

The holding tank actually utilises the liquid hydrocarbons which float to the surface as a “blanket”. This hydrocarbon layer helps prevent vapours from escaping which may cause smell and toxicity to the area surrounding the tank. The hydrocarbon layer should be kept at approximately 600 mm thick; above this is skimmed off to oil slops.

The holding tank should have a bypass line to allow for annual inspection and cleaning. The bottom several centimeters is often pure sludge and should not be allowed to build up or it will continuously flow with the sour water.

Level control inside the holding tank is important to ensure minimal hydrocarbon carryover with the water phase. This is challenging as properly calibrated level control devices are seldom incorporated in the design. The placement of such control devices is also important to ensure proper interface readings. Two of the most common systems for interface measurement involve nuclear signals or sound waves.

The holding tank is the last chance to remove hydrocarbons from the sour water by separation. Any hydrocarbons flowing with the water exiting the holding tank will need to be removed by filtration.

## **Sour Water Conditioning**

Filtration is one of the most basic technologies that can be used to remove suspended matter from the sour water. This however, will only deal with part of the problem (solids). Filtration is not effective in removing hydrocarbons as they tend to form emulsions that can easily penetrate filtration media. For the removal (and often recovery) of emulsified liquid contaminants, the technology of choice is the coalescer. Coalescence is the recombination of two or more small liquids droplets to produce a single entity larger in size. This phenomenon also takes advantage of Stokes Law that relates the velocity of separation of a particle or droplet in a media to the diameter of the contaminant, densities, viscosity and gravitational pull. As coalescence take place, small micron size contaminant droplets coalesce into fairly large droplets resulting in an immediate separation process.

Current practice in many refineries is to employ storage tanks to separate (by gravity) any hydrocarbon and suspended solids from the various comingled sour water streams. However, these systems rarely have sufficient residence time to accommodate effective separation of fine particulate and micro-emulsions (10 microns and smaller). If Stokes law is used to calculate the

required residency time for the separation of a 15 micron emulsion, it will indicate about 2 days. If the particle size is slightly smaller, then the separation time will be in the order of weeks and even months. Based on the low efficacy of residency tanks to properly separate these emulsified contaminants to the level required for feed into the sour water stripper, it is necessary to use secondary systems such as coalescers.

Mechanical coalescing systems are basically comprised of the following three basic technologies:

- inclined plates;
- metal mesh; and
- micro-fiber based.

Due to the particle size and the high fouling properties of emulsified hydrocarbons in sour water streams, only disposable microfiber-based coalescers are able to provide proper emulsion separation. Automatic systems are typically less appropriate as they predominately use metal elements. Other emerging technology options including centrifuges or gas flotation are possible. However, these technologies can be expensive and come with their own sets of issues that need to be carefully evaluated.

Suspended solids removal upstream of the coalescer is mandatory. Particulate removal will protect the coalescer elements and also destabilise the emulsion, significantly improving overall system efficiency. The particle filter and liquid coalescer combination system should be always installed downstream of the sour water charge pump and upstream of the heat exchanger. The system has to be properly designed, sized and fabricated. The correct internals should be selected for the expected water contaminants. The particle filter efficiency and materials have to be compatible with the sour water contaminants and also have to take into account the efficiency of the downstream coalescer.

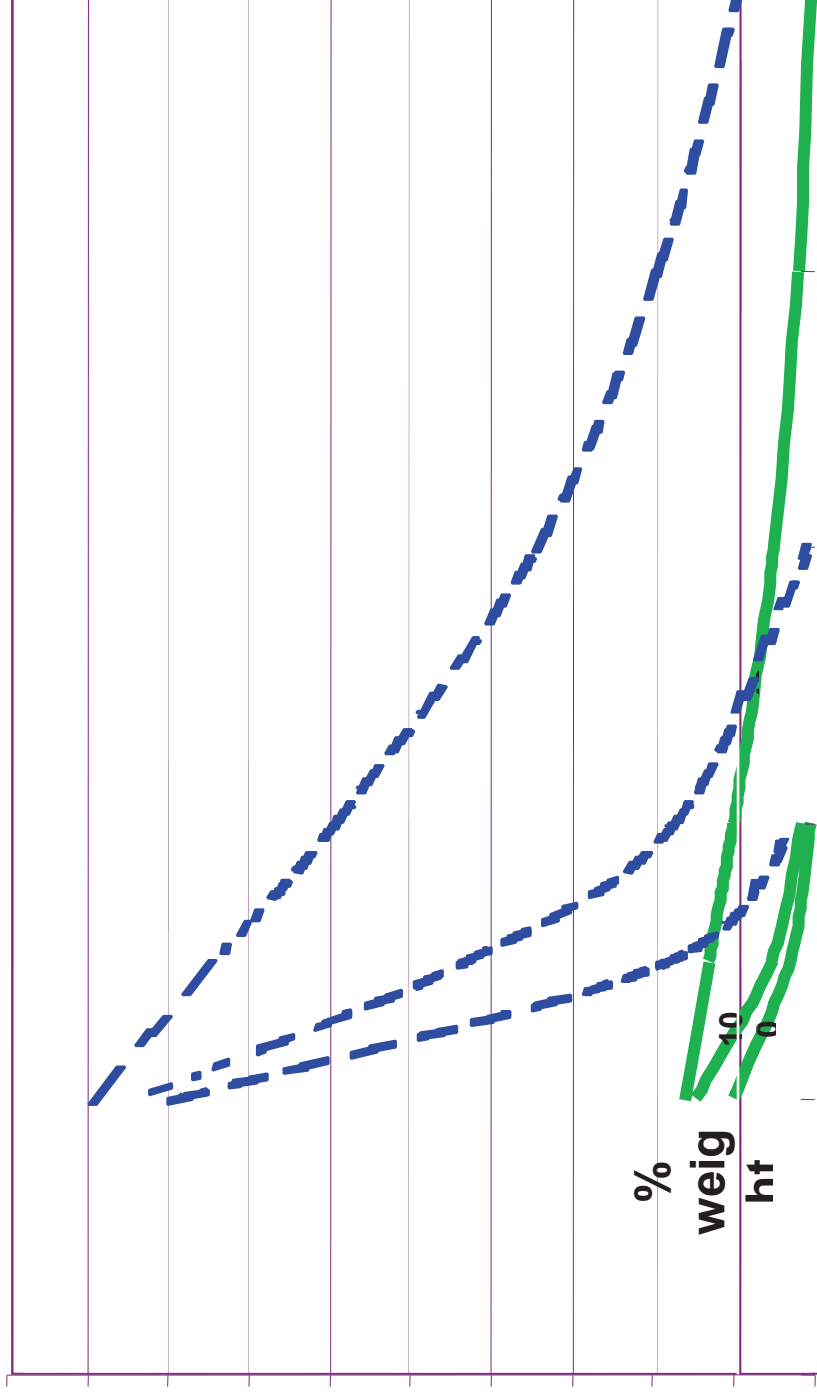
### **Sour Water Stripper Operation**

Once hydrocarbons have entered the stripper, they can either vaporize and travel upwards with the steam, or stay in liquid form and travel down with the water. Neither direction is desirable; however, given the choice, it is better they vaporize, then they can possibly be condensed in the reflux or pump-around system.

Vaporization is accomplished by ensuring there is enough steam flow and temperature in the stripper. Temperature is determined by the pressure of the stripper, which itself is a balancing act; too low a pressure and the temperature is too low (and poor stripping of  $H_2S$  and  $NH_3$  results). Too high and it is very difficult to maintain steam flow, as the demands on the reboiler increase. The end result is that the stripper is often run at the same pressure as the amine regenerator. The acid gases are routed to the same destination (the SRU), therefore, the needed acid gas pressures are the same. The maximum recommended sour water acid gas pressure is 1.4 bar/20 psig. This is more than adequate to push the acid gas to (and through) the SRU, but not enough to cause condensation of steam flow.

The recommended steam flow (either live steam, or, preferably, to a reboiler) depends on the number of contact stages in the tower. The more contact stages, the less steam flow is required, as shown in Figure 6 below:

Figure 6: Steam versus theoretical stages



Most sour water strippers are 10 or 15 stages (which in reality is approximately 30 trays or 18 to 20 m of packing), therefore they require between 10 and 15 percent weight steam on feed in order to strip the  $\text{H}_2\text{S}$  and  $\text{NH}_3$  out of the water. This is equal to 100 – 150 kg/steam per  $\text{m}^3$  of water flow.

The stripper will have a cooling section at the top, whether a refluxed set up or pump-around, which should reduce the acid gas temperature to  $85^\circ\text{C}$ . Cooling the overhead steam flow will reduce the amount of water and hydrocarbon in the SWAG. The recommended SWAG temperature is  $85^\circ\text{C}$  based on always being above the sublimation point (temperature at which a change from solid to gas occurs directly) of the various salts that are potentially present. Salts should not be allowed to deposit as they will plug the line feeding the SRU. Particularly in refineries treating water from an FCC system the SWAG the temperature should not drop to below  $85^\circ\text{C}$ , because salts that form when ammonia reacts with  $\text{CO}_2$  have higher sublimation points compared to salts formed with  $\text{H}_2\text{S}$ :

- Ammonium bisulphide,  $\text{NH}_4\text{SH}$ :  $45^\circ\text{C}$
- Ammonium carbonate,  $(\text{NH}_4)_2\text{CO}_3$ :  $75^\circ\text{C}$
- Ammonium bicarbonate,  $\text{NH}_4\text{HCO}_3$ :  $75^\circ\text{C}$

It is true that operating a cooler SWAG would condense more hydrocarbons in either the reflux or the pump-around system, thereby reducing the hydrocarbon content in the acid gas. However, the risk of fouling due to salt deposition is too high. A temperature of  $85^\circ\text{C}$  provides an acceptable safety margin in case there is any cooling along the pipeline to the SRU (certainly the SWAG pipeline should be well insulated and steam traced). With any significant increase above  $85^\circ\text{C}$  though, the amount of water and hydrocarbon in the SWAG will increase unnecessarily.

Any hydrocarbons condensed in the overhead system should be skimmed off, especially in the case of a refluxed system where the overall volume of water is much lower than in a pump-around. The skimming can be done in the reflux accumulator.

## REFERENCES

- E. van Hoorn, *“Basics of Sour Water Stripping”*; Amine Processing textbook, published by Sulphur Experts, 2002-2012
- B. Klint, *“Hydrocarbon Destruction in the Claus SRU Reaction Furnace”*, Sulphur Recovery textbook, published by Sulphur Experts, 2005-2012

## **Appendix J**

### **Hydrocarbon Contamination of Amine Systems**

## Hydrocarbon Contamination of Amine Systems

Hydrocarbons in amine acid gas are known to cause process issues in downstream Sulphur Recovery Units (SRUs). Some of the upsets that led to emissions exceedances were caused by hydrocarbon in the acid gas entering the SRUs, so understanding how hydrocarbons end up in the acid gas and how they can be controlled will play a vital role in reducing hydrocarbon-related SRU trips.

The aromatic BTEX hydrocarbon species are especially difficult to combust, and they burn with a sooty flame that fouls downstream catalyst beds. Destruction of BTEX requires high SRU reaction furnace temperatures ( $>1925^{\circ}\text{F}$ ). Many facilities have difficulty operating their SRU reaction furnaces at these elevated temperatures. As such, there is strong operational and legislative motivation to minimize the volume of hydrocarbons in the acid gas and in the amine system.

Reducing hydrocarbons in amine systems is advantageous to not only the sulphur plant, but also within the amine system itself. Hydrocarbon contamination of amine can result in foaming, fouling and destruction of gaskets in plate and frame lean/rich exchangers. Hydrocarbons in amine also represent lost production for the refinery. Amines are not meant or designed to remove hydrocarbons, which are the components of natural gas (or Liquefied Petroleum Gas (LPG)), which are used as fuel or sold.

### AMINE SWEETENING PROCESS

Using alkanolamines for acid gas removal is a process that has been in use since 1931. Simplistically, an amine system absorbs  $\text{CO}_2$  and  $\text{H}_2\text{S}$  contaminants out of a gas or LPG stream in a contactor unit (often called an absorber) at high pressure and low temperature and binds the contaminants to an amine molecule through a set of chemical reactions. The binding reaction is then reversed in a stripper unit (regenerator) at low pressure and high temperature. The  $\text{CO}_2$  and  $\text{H}_2\text{S}$  loaded amine (referred to as 'rich' amine) is thus regenerated for reuse, and the  $\text{CO}_2$  and  $\text{H}_2\text{S}$  exit the system via the acid gas stream and, in the Limetree Bay refinery, flow to the SRU 3 or SRU 4 sulphur recovery units (see Figure 1).

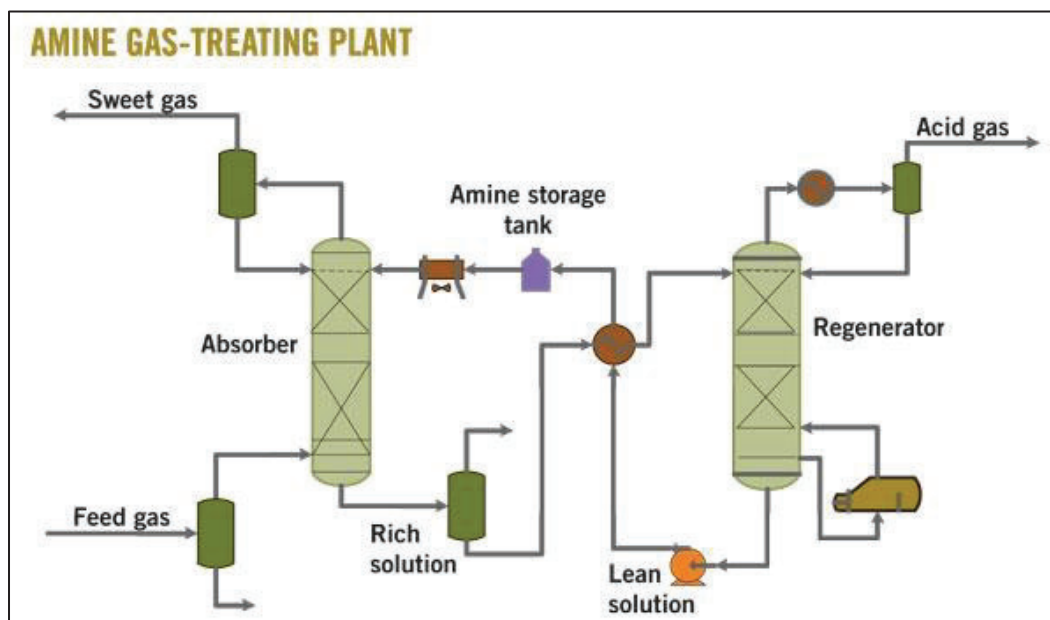


Figure 1. Generic Amine Plant

Other than some specialty applications, the inlet gas to most amine absorbers will contain a variety of hydrocarbons. Most gas-phase hydrocarbons will remain as gas and flow harmlessly up through the amine and exit out of the top of the tower. Liquid hydrocarbons in LPG treaters will initially mix with the amine, then separate if enough residence time is given to the amine in the bottom of the treater. In a gas-liquid contactor, very little separation time is included in most designs and, therefore, any liquid hydrocarbon ingress will travel with the rich amine. If the rich amine entering the regenerator contains hydrocarbons, the hydrocarbons will then vaporize and travel with the acid gas. If the acid gas is routed to a sulphur plant, the hydrocarbons can create problems, both operationally and mechanically. In the experience of Sulphur Experts, Amine Acid Gas (AAG) containing more than 2% hydrocarbon is an indication of problems upstream of the stripper.

The next section discusses how to mitigate hydrocarbons in the rich amine feeding the regenerator, which reduces fouling, foaming, corrosion, and many associated operating problems both in the Amine Regeneration Unit (ARU) and the SRU.

## HYDROCARBONS IN AMINE

Hydrocarbons will first enter the amine system in the contactor. Any hydrocarbons that end up in the rich amine will arrive there either by absorption (solubility), entrainment, condensation or emulsification. Amines are organized into three categories: primary, secondary and tertiary. A paper published by Critchfield *et al.* [4], explained how hydrocarbon solubility in amines relates to the molecular weight of the amine. The order of hydrocarbon solubility, in order of lowest to highest is as follows:

- **Monoethanolamine (MEA)** (former amine in ARU 4 and ARU 5)
- Diglycolamine (DGA)
- Diethanolamine (DEA)
- **Methyldiethanolamine (MDEA)** - existing amine in ARU 6 and 7, but new to ARU 4 and ARU 5
- Diisopropanolamine (DIPA)

The use of MDEA throughout the refinery will have an effect on the quantity of hydrocarbon in the acid gas feeding the SRUs, because of the higher solubility in the solvent. Operations staff reported noticing a change in how the system reacted to previously successful operating parameters that would reduce the hydrocarbon content in the acid gas. The units took much longer to reduce hydrocarbon contamination with MDEA as a solvent compared to the former amine, MEA.

There are two main types of hydrocarbons that can enter an amine plant: polar and non-polar. Non-polar hydrocarbons are generally free hydrocarbons, which do not blend well with amines and can be relatively easily separated and removed. Polar hydrocarbons have a unique chemical characteristic, whereby part of the molecule is hydrophobic, and the other part is hydrophilic. Contamination of a polar hydrocarbon results in an emulsion of amine and hydrocarbon. If the level of contamination is high enough in the amine, significant amounts of hydrocarbons (being pulled along by the surfactant) are carried with the solution to the flash tank.

Although slightly different in chemistry, aromatics (i.e., BTEX) exhibit characteristics similar to polar hydrocarbons, and are even more harmful to the SRU. The thesis of Borda [1] provides a good review of the available data on BTEX and VOC solubility in amine solutions.

Figure 2 is an example of different levels of hydrocarbon contamination that can occur within the same system. These samples were all taken from individual contactor rich amine outlets at the same refinery.



Figure 2. Amines Contaminated With Varying Degrees of Hydrocarbon

Hydrocarbons in rich amine streams can be present essentially in the following three forms:

- **Free Hydrocarbons.** These non-polar hydrocarbons will float on top of the amine solution within a few minutes if given the chance. This typically occurs in the flash tank or the bottom of the various absorbers.
- **Soluble Hydrocarbons.** All hydrocarbons will have certain solubility in amine solutions. The extent of the solubility will depend on the following:
  - Type and concentration of amine (common hydrocarbons such as  $C_1/C_2/C_3$  are two to three times more soluble in amine compared to pure water,
  - pH of the amine,
  - Amine contactor pressure and temperature, and
  - Type of hydrocarbon and polar functional groups such as carboxylic acids and alcohols. Aromatics are included in this group, as is explained further in this paper. Benzene is six times more soluble in amine than another straight-chain 6-carbon saturated hydrocarbon like hexane.
- **Emulsified Hydrocarbons.** When surfactants are present, hydrocarbon contaminants can form very small droplets in the amine solutions. These droplets are stabilized by molecular surfactants (similar to soaps or detergents) and also by small size suspended solids. Emulsion droplet sizes can range from a few microns to about 500 microns. Micro-emulsions, which are the most stable emulsions available (and can take weeks to separate) are typically found when droplet sizes are < 10 microns.

Figure 3 shows the difference in appearance between the three forms of hydrocarbon in rich amine solutions.



**Figure 3. Free (left), Soluble (middle) and Emulsified Hydrocarbons (right) in Amine**

### **EFFECT OF HYDROCARBONS ON THE SULPHUR PLANT**

Preventing hydrocarbons from entering the sour water stripper or the amine absorbers will in turn prevent hydrocarbon rich acid gas from entering the sulphur plant (SRU). There are several reasons why it is advantageous to minimize hydrocarbon in the SRU feed, the most important involving:

- Difficulties maintaining stable operation;
- Decreased capacity;
- Lower efficiencies; and
- Potential issues with catalyst deactivation and sulphur quality due to soot.

Sulphur plants require combustion air in the main reaction furnace to oxidise part of the  $H_2S$  contained in the feed gas to form  $SO_2$  prior to entering the downstream catalytic stages of the modified Claus process. The modified Claus process is a reversible reaction, and its success is highly dependent on reacting two moles of  $H_2S$  with one mole of  $SO_2$  to form sulphur and water. Having either too much  $H_2S$  or too much  $SO_2$  will limit the equilibrium conversion of the catalytic stages and impact the overall sulphur recovery efficiency of the SRU.

$SO_2$  is formed in the reaction furnace by the combustion of air and  $H_2S$ . However, since some  $H_2S$  is still needed for the downstream reactions, the air flow rate to the reaction furnace is controlled such that only *a portion* of the  $H_2S$  is combusted to  $SO_2$ , resulting in a sulphur plant furnace that operates in a reducing environment; this makes the air flow to the furnace a critical control parameter.

To control the air flow, most sulphur plants use a set air-to-feed gas flow (or mass) ratio which controls the majority of the air flow rate to the SRU and is dependent on the feed gas flow rate. This is, however, a very basic type of flow control, and on its own is not enough to ensure maximum performance from the Claus plant. In order to maintain a proper  $H_2S/SO_2$  ratio in the Claus tail gas, an analyser is used to

measure the  $\text{H}_2\text{S}$  and  $\text{SO}_2$  concentrations at the tail gas and thus fine-tune the air flow rate to the reaction furnace. Unfortunately, due to the location of this analyser at the back-end of the process, a certain amount of lag time is inherent in this control system. Since a small amount of hydrocarbons consume a large amount of oxygen in the reaction furnace, this directly impacts the formation of  $\text{SO}_2$ , and if these changes in composition occur quickly and rapidly, then this can result in significant operating problems for the SRU. Ideally, air flow should be controlled within  $\pm 0.5\%$  of that necessary to maintain a 2:1  $\text{H}_2\text{S}$ -to- $\text{SO}_2$  ratio in the Claus tail gas.

As the concentration of hydrocarbons increases, so does the amount of air required to combust them. The heavier the hydrocarbon, the more air required. Therefore, even very small amounts of heavy hydrocarbons ( $\text{C}_6+$ ) can result in a significant air demand. Most sulphur plants are limited by the air blowers to deliver sufficient amounts of air, adding anything to this process that competes for oxygen will limit the amount of sulphur that can be processed in an SRU.

As seen in Figure 4, the air flow rate for a simple acid gas increases by 10% with the addition of 2% light hydrocarbons ( $\text{C}_1$  and  $\text{C}_2$ ), and adding increasingly more and heavier hydrocarbons (i.e., equal amounts of  $\text{C}_1 - \text{C}_6$ ) can double the air required to combust them. This increase in the air requirement will reduce the processing capacity of a sulphur plant. In addition, hydrocarbons in the feed gas will increase the formation of  $\text{CS}_2$  in the reaction furnace and decrease the partial pressure of  $\text{H}_2\text{S}$  and  $\text{SO}_2$  in the system. This will reduce the equilibrium conversion rates of  $\text{H}_2\text{S}$  and  $\text{SO}_2$  in the catalyst beds, thus reducing the overall efficiency. In addition, the higher  $\text{COS}$  and  $\text{CS}_2$  formation rates in the reaction furnace also require higher first converter operating temperatures and/or the use of specialized catalyst to convert these compounds back to  $\text{H}_2\text{S}$ . They otherwise contribute to significant efficiency losses in a sulphur plant, which has an impact on operating costs and equipment sizing.

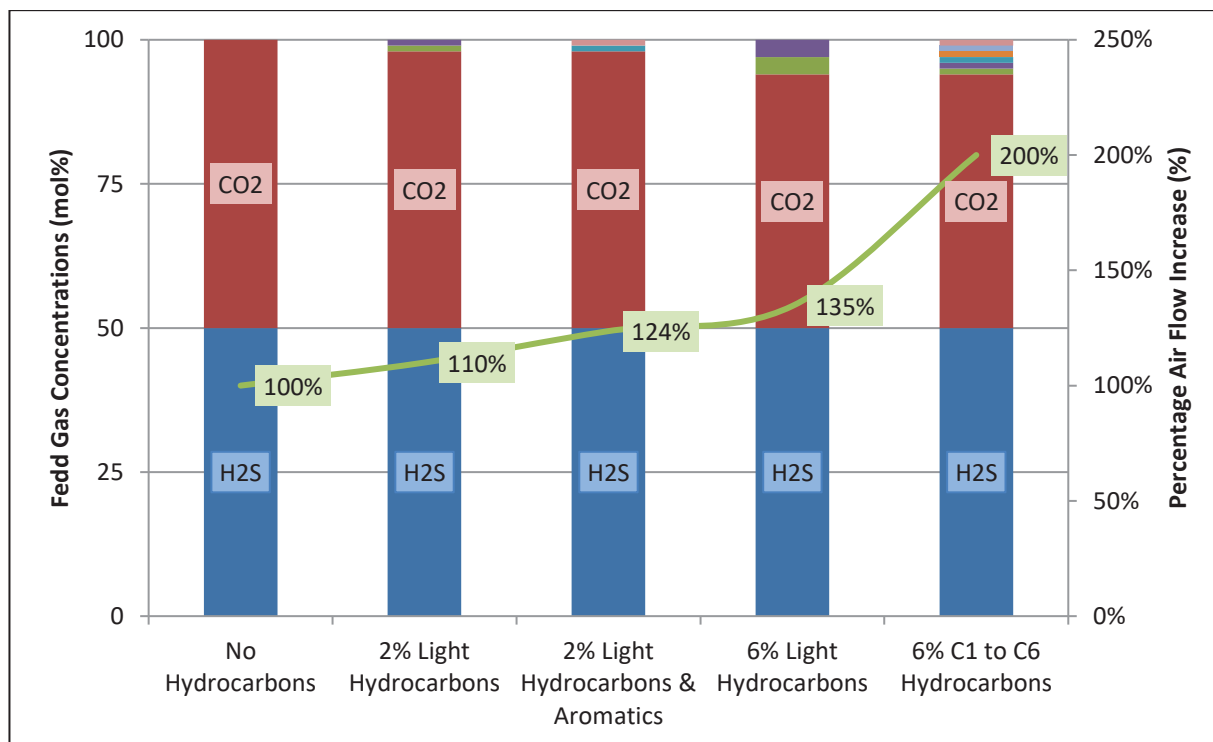


Figure 4 - Air Flow Requirement for Various Feed Gases

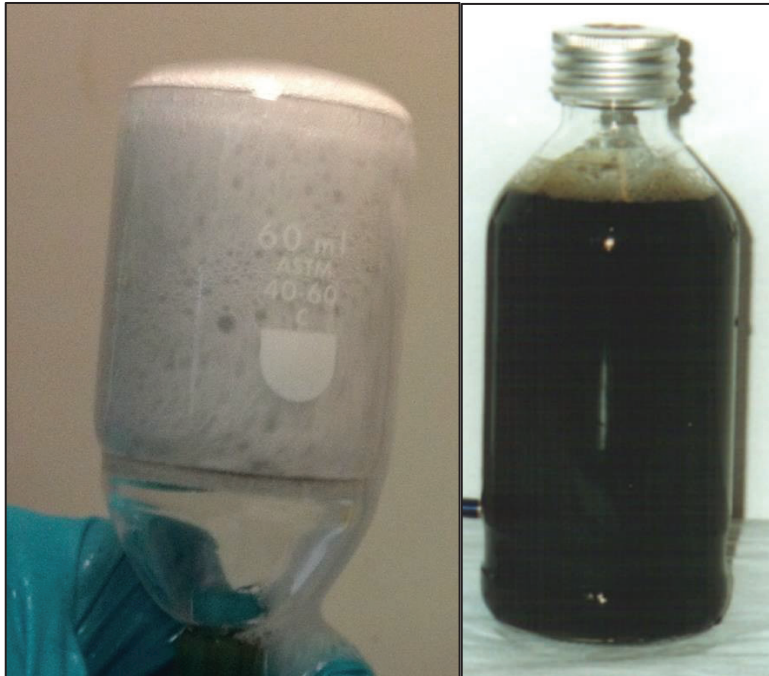
## EFFECT OF HYDROCARBONS ON THE AMINE PLANT

Hydrocarbons do not chemically bond to the amine, so there is no direct harmful effect on the actual amine solution. Given the right amount of time, or use of technology, any hydrocarbons mixed into the amine can be removed and the amine can then be reused. In the meantime, however, while a mixture of hydrocarbon and amine is circulating through the plant, many negative consequences can result; the most common being as follows:

- **Foaming.** The first and foremost concern when amines are contaminated with hydrocarbons is foaming. Hydrocarbons have a lower surface tension than amine, which allows the surface of the liquid to expand quite easily. When gas or steam is bubbled through the amine, the bubble reaches the surface of the liquid, but does not 'pop'. The bubble remains, and more and more bubbles build up on top of it until the entire vapour space is filled with this foam as illustrated in Figure 5. Foaming can be a concern in both the contactor and the regenerator.

When amines foam in the contactors, they not only stop removing  $H_2S$  from the gas, but can also carry more hydrocarbons out the bottom of the tower (gas carry-under) resulting in excess flash gas and, potentially, more hydrocarbon in the acid gas feeding the SRUs. This extra flashed hydrocarbon fraction is fed to the GRU2 contactor, where it again has an opportunity to be absorbed by the amine and end up in the feed to the SRU.

- **Fouling.** Hydrocarbons contribute to the black shoe polish that commonly fouls amine filters, lean/rich exchangers and packed towers (see Figure 6). A carbon bed is used to remove hydrocarbons, but because the carbon is generally on the lean side, the amine has to flow through many pieces of equipment beforehand, where hydrocarbons can form a matrix along with iron sulphides, degraded amine, and antifoam. This is what fouls amine systems.
- **Gasket Destruction of Plate and Frame Exchangers.** There are several different types of gaskets available for separating the plates in plate and frame exchangers. None of these gaskets are immune to the harmful effects of hydrocarbons flashing across the exchanger. Liquid hydrocarbons can cause polymerization of the gasket material and flashing hydrocarbons can erode the gaskets. Operators must rely on the flash tank to minimize the content of the rich amine entering the exchanger. The Limetree Bay Refinery does not have Plate/Frame exchangers.
- **Loss Of Treated Product.** Hydrocarbons in amine represent a loss of hydrocarbons in the treated gas (i.e., result in lower volumes of fuel gas or LPG). These losses directly impact the profitability of the gas plant or refinery and are obviously undesirable.



**Figure 6. Foaming Tendency of Hydrocarbon Contaminated Amine**



**Figure 7. Black Shoe Polish on Rich Amine Filters**

#### **MINIMIZING HYDROCARBON CONTENT IN AMINE ACID GAS**

The best way to minimize hydrocarbons in amine acid gas is to ensure that excess hydrocarbon does not enter in contact with the amine solution in the first place. This requires a comprehensive and thorough evaluation of the inlet gas stream to each amine contactor in the system. Typical amine plant designs will include at least an inlet separator before the contactor to knock out free liquids. However, many of these inlet separators are inadequate for complete hydrocarbon liquid removal.

Other options for minimizing the hydrocarbon content of the amine acid gas include the following:

- **Option 1.** Optimizing the operation of the actual amine plant.
- **Option 2.** Optimizing the amine flash drum operation. Sometimes design changes to the drum interior may be necessary to ensure minimal hydrocarbon breakthrough.
- **Option 3.** Using filtration and/or coalescing technology on the rich amine to remove hydrocarbons.
- **Option 4.** Using potential skimming capabilities on contactor, flash tank and reflux water.
- **Option 5.** Technological solutions.

### Option 1: Optimization of The Amine Plant Operation

Once the plant is designed, built and operating, there are two strategies operators can employ to minimize the level of hydrocarbon pick up by the amine:

- a) preventing hydrocarbon entering the contactor with the sour gas in the first place, and
  - b) operating the plant at conditions that minimize hydrocarbon solubility in amine, noting that examples include choice of amine type and strength, circulation rate, rich loading, differential temperature between lean amine and inlet gas, and reflux operations.
- **Preventing Hydrocarbon Ingress.** Assessing the amount of hydrocarbon entrainment in gas can be directly analyzed. Several companies perform entrainment testing at moderate costs. When done correctly, the associated optimizations that are possible as a result of the new data rapidly pays back the cost of the testing. The resulting changes that are made to process conditions can ensure reliability, integrity, capacity and energy/chemical utilization, thereby resulting in valuable cost savings to the plant.

Bulk liquid hydrocarbons are meant to be removed from inlet gas streams by the inlet separator. More precision removal can be done using a cyclone separator and/or a coalescing filter. The inlet separator is the most important piece of equipment as far as hydrocarbons in amine acid gas are concerned - if the inlet separator fails, there will be serious consequences for the sulphur plant. Cyclones, centrifuges and coalescers are primarily used to prevent foam promoting contaminants from entering the amine contactor, which is of course important, but will not necessarily make much of an impact on the level of hydrocarbons in the AAG.

Inlet separators rely on four basic parameters which determine the effectiveness of liquid separation from gas:

- **Density Difference between the Liquid and Gas.** Higher density liquids will be removed easier from gas than lighter ones because of the lack of gas solubility in the hydrocarbon. The two phases want to separate.
- **Flow Directional Change.** Flow direction changes are possible for the gas, but not so much for the droplets of liquid. Forcing the gas around an impingement plate followed by a demister pad in the top of the vessel creates something similar to an obstacle course. The gas can go through it, but liquid droplets impinge on the surface of the obstruction and eventually build in size until the droplets fall to the bottom of the separator. Figure 9 is a typical inlet gas separator, with a diverter plate and demister pad for flow directional change.

- **Velocity.** Velocity has a large effect on the volume of liquid hydrocarbon in a gas stream. The velocity of the gas stream imparts drag force on each liquid droplet, pulling the droplet along the pipe. The only opposing force to counter this is gravity. It is important that gas velocities not be so high that they overcome gravity. Gas flow, as well as gas pressure, determines the velocity through the piping. This is why a separator has to be carefully designed to minimize pressure drop across the vessel, since a drop in pressure results in the gas expanding and a corresponding increase in velocity and drag force.
- **Time.** Time is the final separation parameter. It takes time for gravity to pull droplets out of a gas stream. Therefore, a larger separator tends to remove more liquids than a smaller vessel, assuming proper design of each.

Proper operation of an inlet separator involves ensuring the liquid level is kept low at all times. The frequency of the level control valve opening should be noted, since frequent dumping of the vessel could mean an excessive amount of liquids having to be removed from the gas stream. This could indicate that there is a possible problem upstream that requires investigation.

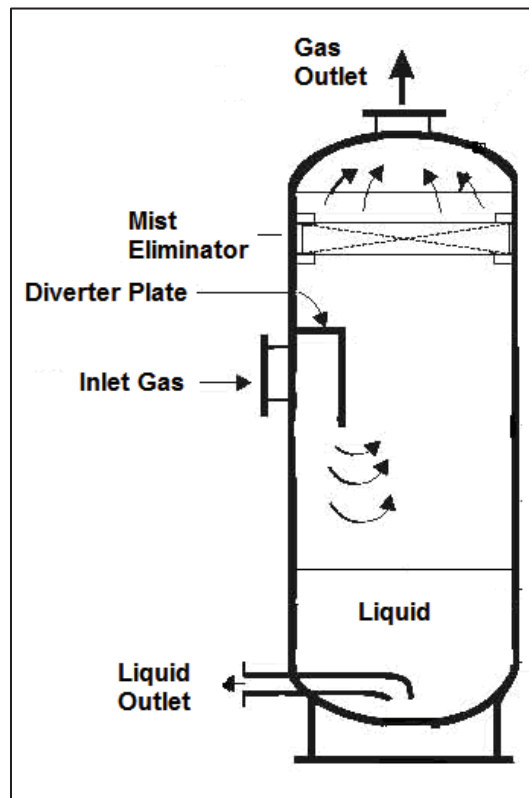


Figure 8. Typical Inlet Gas Separator

Separators should always operate with a low and consistent pressure drop. Low pressure is required to prevent excessive drag forces on liquid droplets and consistent pressure is to ensure that there is no fouling or plugging of the demister pad within the vessel.

- **Plant Operating Conditions.** There are several operational parameters that directly affect the amount of hydrocarbon in amine acid gas:
  - **Amine Circulation Rate.** Because of the inevitable solubility of hydrocarbons in amine (described earlier), a higher amine circulation rate will carry more hydrocarbons into the circulating rich solution. Furthermore, higher amine circulation rates decrease the flash tank residence time, lowering the hydrocarbon removal efficiency.
  - **Amine Rich Loading.** By increasing the loading (aqueous CO<sub>2</sub> and H<sub>2</sub>S amine salt concentration) of the amine solution, less amine and water is available for interaction with the charged part of the hydrocarbon. This renders the hydrocarbon-hydrocarbon interactions stronger than the amine-hydrocarbon interactions, causing the hydrocarbon molecules to coagulate through hydrophobic interactions with one another. The fact that higher rich loadings reduce the amine-hydrocarbon solubility levels is even further reason to lower the amine circulation rate, if possible.
  - **Amine Strength.** Since water naturally repels hydrocarbons, the lower the amine concentration in the aqueous blend, the lower the hydrocarbon solubility. The former MEA blend operated at only 18-20 wt% strength, whereas the MDEA strength is in excess of 30 wt% (typically 40-50 wt%), so hydrocarbon solubility in the rich amine is greater than before the refinery re-start.
  - **Differential Temperature between Lean Amine and Inlet Gas.** Before gas streams enter the amine contactor, the gas streams pass through an inlet gas separator, which allows for liquid hydrocarbons to be separated. Therefore, the gas leaving the separator should be at the hydrocarbon dewpoint, meaning if the gas pressure were to increase or the temperature to decrease, hydrocarbons would condense out and form droplets in the gas line. It is important to not allow this to occur as it will result in liquid hydrocarbons in the rich amine.

For this reason, it is recommended the inlet gas separator be located within 30 ft of the amine contactor, which will minimize the risk of condensation of hydrocarbons along the pipeline. It is also recommended that this line be insulated.

It is also possible for hydrocarbons to condense inside the actual amine absorber, which can happen if the gas is cooled while travelling up the contactor. This will happen if the lean amine being injected into the contactor is cooler than the inlet gas stream. In fact, because the hydrocarbon dewpoint of the gas changes as acid gases are removed (because of the removal of acid gases, the hydrocarbon dewpoint temperature will be higher at the top of contactor as compared to the bottom), it is recommended that operators maintain a minimum five Fahrenheit degree temperature differential between the lean amine and the inlet gas.

- **Reflux Operation.** Despite optimizing amine circulation rates, rich loadings and flash tank operations, there will still likely be hydrocarbons entering the regenerator. The last area where hydrocarbons can be removed before leaving with the acid gas is in the reflux system. Proper condensing of the regenerator overhead stream will minimize the level of hydrocarbon vapour and the hydrocarbons will instead circulate with the reflux. The recommended reflux temperature is between 95 to 115°F.

Refiners tend to run on the higher end of this range to minimize the risk of ammonia salt precipitation. Gas plants, or systems with no ammonia ingress, should target lower reflux temperatures.

Since hydrocarbons are condensed in the reflux, the concentration will increase if there is no reflux purge. An increase in hydrocarbon content in the reflux is undesirable, as this increases the risk of hydrocarbon carryover with the acid gas and can also cause foaming and other operational problems in the regenerator. Hydrocarbon contaminated reflux streams should be either continuously purged to a sour water stripper or disposal tank. If purging is not available, completely emptying the reflux drum to disposal is acceptable. This should be done based on visual or laboratory analysis of reflux water (or better yet reflux skimming) for hydrocarbons.

It is important to recognize the implications of operating outside the recommended reflux temperature range. Specifically, operating at less than 95°F will not only have limited effect on the amount of water and hydrocarbon in the acid gas, but also increases the necessary reboiler duty since the cold reflux will be condensing an inordinate amount of steam traffic in the upper section of the regenerator. Operating at higher than the recommended reflux temperature will allow excessive water and hydrocarbon to escape with the acid gas, negatively affecting SRU operations as well as increasing the make-up water demand on the amine plant.

## **Option 2: Amine Flash Tanks**

Separation technologies based on pressure drop, velocity changes and residence time are among the most common separation systems used in oil and gas operations. All these technologies have the common theme of using simple concepts to attempt to solve a separation problem. One such example is the amine flash tank. This device removes off-gases by reducing the rich amine pressure downstream of an amine contactor.

If designed correctly, these systems also provide limited liquid-liquid separation capabilities for free hydrocarbon removal since these hydrocarbon liquids will float to the top of the amine solution within 30 minutes and can then be skimmed. No emulsified or dissolved contaminant is affected.

For a flash tank to effectively separate hydrocarbons from amine, there must be sufficient residence time as well as sufficient pressure reduction. Entrained hydrocarbon gases will flash off within three to five minutes, noting that the lower the flash tank pressure, the faster and more efficient hydrocarbon gases will flash.

Flash tank pressure is determined by the necessary flash gas and rich amine pressures. Common flash gas destinations include the following:

- Low pressure fuel gas absorber inlets
- Flare
- Incineration
- Acid gas

The rich amine must leave the flash tank and flow through the following:

- Rich amine filters (if they exist)
- Lean/rich exchanger
- The vertical piping up to almost the top of the regenerator

Generally, 70 psig is enough pressure to push both the gas and amine to their respective destinations. It is important to not pressure the flash tank any higher than necessary since this will reduce the amount of hydrocarbon flashing. If the flash gas is routed to an extremely low pressure flare or incinerator, some plants will operate the flash tank at virtually atmospheric pressure and will install rich amine pumps immediately after the flash tank in order to push the amine through the exchanger to the regenerator.

Flash tank residence time is a function of the size of the vessel, the level at which the amine is maintained inside the vessel, and the circulation rate of the amine. If the tank is designed only for two-phase separation, the tank will simply be an open tank with a gas outlet in the top and liquid drain at the bottom. Operators should set the level at 50 to 60% full. This maximizes residence time, while still allowing for vapour disengaging space, noting that when hydrocarbons flash from liquid to gas, the hydrocarbons expand in size by up to 300% and can therefore carry gas upwards as a result of high velocities. Having at least 40% of the tank as vapour space will allow for gravity to pull the droplets of that amine back out of the flash gas and into solution.

For designers, sizing a 30 minute residence time is often achieved by assuming some variables in the Stokes Law calculations, such as hydrocarbon density and hydrocarbon droplet size. The typical values for these tend to be a specific gravity of 0.6 to 0.7 and droplet sizes of 150 microns and larger. It is important to note that these values do not account for the possibility of heavier hydrocarbons and micro-emulsions that exist in rich amine streams.

The Stokes Law calculations also do not account for any possible surfactant contaminants, which aid in stabilizing micro-emulsions. Granted, designers must balance the size and cost of the flash tank with expected performance. Designing a flash tank for 10-micron droplet removal would make the flash tank so large that it would not be economical to build or fit within the battery limits of the unit.

Assuming the residence time is adequate, any free hydrocarbons floating on the amine surface can and should be skimmed. Depending on the flash tank design, these hydrocarbons may flow over a weir or into an internal bucket that is attached to the inside of the vessel walls. When skimming, it is preferential to be able to sample the skimmed liquid to ensure it is indeed hydrocarbon and not amine. Some skimming sections have site glasses where the interface between amine and hydrocarbon can be seen. These make it very simple for operators to prevent the skimming of amine to disposal.

A number of different flash tank designs are available, some certainly more effective than others. A growing trend is to incorporate metal mesh internals to promote coalescence, which can compensate for low residence times. These promising systems so far have provided marginal results because of poor understanding of highly fouling rich amine streams. Most flash tanks, whether two or three-phase separators, are often sized based on correct parameters, but can lack the understanding of liquid and solid contaminant loading.

### Option 3: Rich Amine Liquid/Liquid Coalescers

Presently, many amine units only separate hydrocarbons in the flash tank. It is commonly believed that flash tanks will be able to separate any hydrocarbon in the rich amine streams. This is correct to some extent; however, the reality is that emulsions in rich amine streams are very stable, with droplet sizes near or less than the micro-emulsion range (10 microns and smaller). If Stokes law is used to calculate the required residence time for the separation of a 15-micron emulsion, the result will indicate approximately two days. If the particle size is slightly smaller, then the separation time can be in the order of weeks or even months. Based on the low efficacy of residence vessels (flash drums) to properly separate these emulsified contaminants to the level required for feed into the regenerator, it is necessary to use secondary systems, such as coalescers.

Coalescence is the recombination of two or more small liquid droplets to produce a single droplet that is larger in size. This phenomenon also takes advantage of Stokes Law, which relates the velocity of separation of a particle or droplet in a medium to the diameter of the contaminant, densities, viscosity and gravitational pull. As coalescence takes place, small micron size contaminant droplets coalesce into fairly large droplets, resulting in an almost immediate separation from the continuous phase.

Mechanical coalescing systems are basically comprised of the following three technologies:

- Inclined plates
- Metal mesh
- Microfiber based

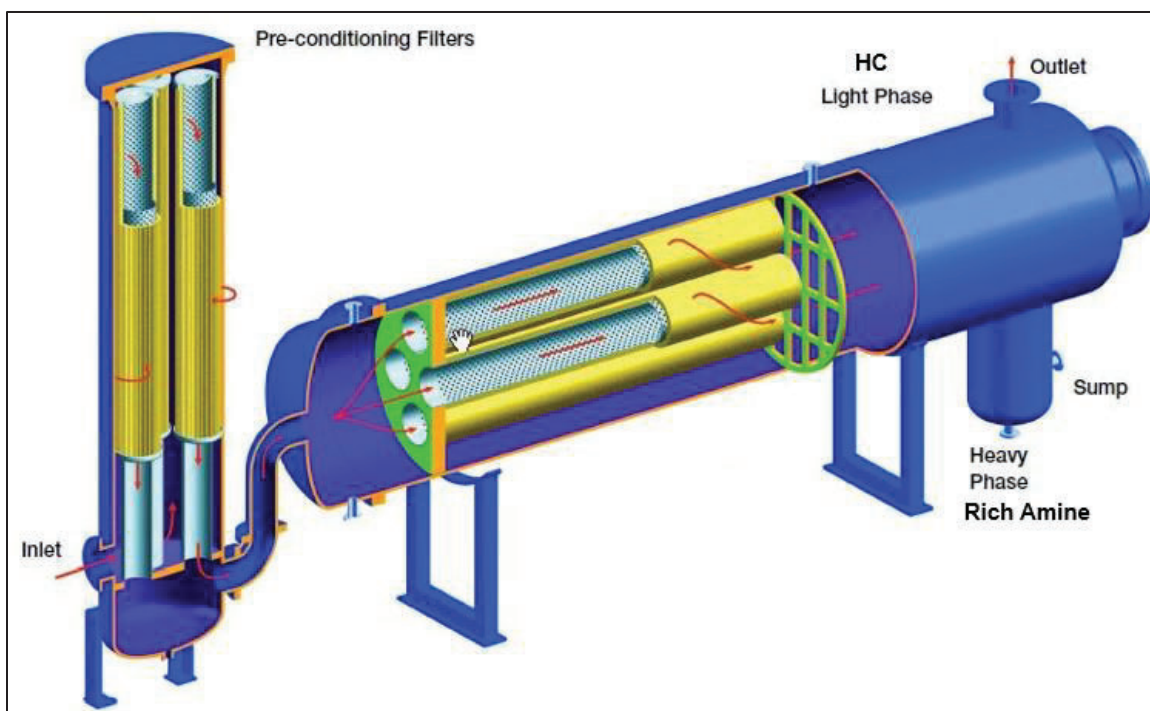
Because of the particle size and the high fouling properties of the solids and emulsified hydrocarbons in rich amine streams, only disposable filters and microfiber-based coalescers are able to provide the proper particle removal and emulsion separation.

Suspended solids removal upstream of the coalescer is mandatory. Particulate removal will protect the coalescer elements and will also help destabilize the emulsion. If solids are introduced into a coalescing filter, it will plug off almost immediately and become ineffective.

Liquid-liquid coalescers are devices designed to separate small, emulsified liquid contaminants in a liquid stream. These devices are segregated into the following two general categories:

- Low efficiency systems with metal-based internals
- Coalescers with microfiber internals

The two types of coalescers perform rather differently and should be used for different objectives and specific cases. While metal-based internal coalescers are effective for separating free liquids and macro emulsions (~100 microns and larger), coalescers with microfibers are more suited for separating micro emulsions (100 microns and smaller). Figure 9 shows the set-up for a liquid/liquid coalescer that would be installed on the outlet of the flash drum and ahead of the lean rich exchangers.



**Figure 9. Liquid / Liquid Coalescer**

#### **Option 4: Use of Skimming Devices**

Hydrocarbons that float to the surface of amine or reflux water may be skimmed, assuming the design of the vessel allows for skimming. Most flash tanks have skim connections or hydrocarbon carryover weirs included in the design. Some contactors, reflux accumulators and regenerators also have skim connections. Whenever possible, hydrocarbons should be skimmed out of the system in order to prevent any chance of evaporation. Areas with higher residence times, such as flash drums and regenerator bottoms have the potential for particularly high hydrocarbon volumes.

Although not commonly thought of being a “filter”, the regenerator absolutely will drive hydrocarbons out of the amine, in effect filtering the solution. The vaporized hydrocarbons enter the reflux system where the hydrocarbons are possibly condensed in the reflux and where if not removed, will eventually be recycled back to the regenerator with the reflux water. Reflux water that is contaminated should therefore be partially purged, or better yet skimmed.

Figure 10 shows hydrocarbons floating on the water phase of the reflux drum from ARU 7. This is a common sight in hydrocarbon-contaminated amine systems. Typically, the reflux water will be clear and transparent water, and sometimes it has a milky white emulsion appearance (as the bottom water portion indicates), but when there is enough hydrocarbon to make a visible floating layer, then it will be very difficult to prevent carryover to the SRU.

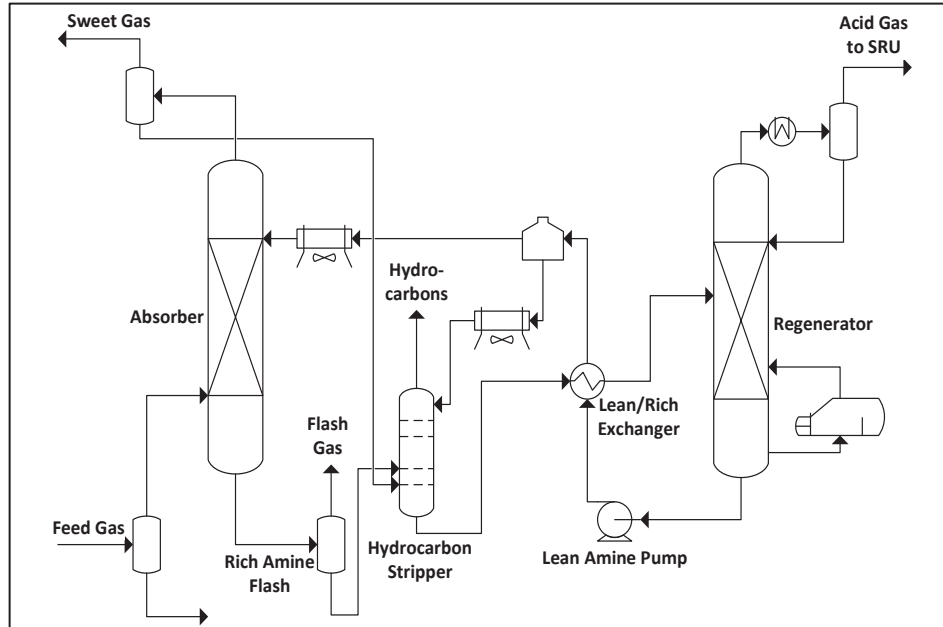


**Figure 10. Reflux Water with Skimmable Hydrocarbon – ARU 7**

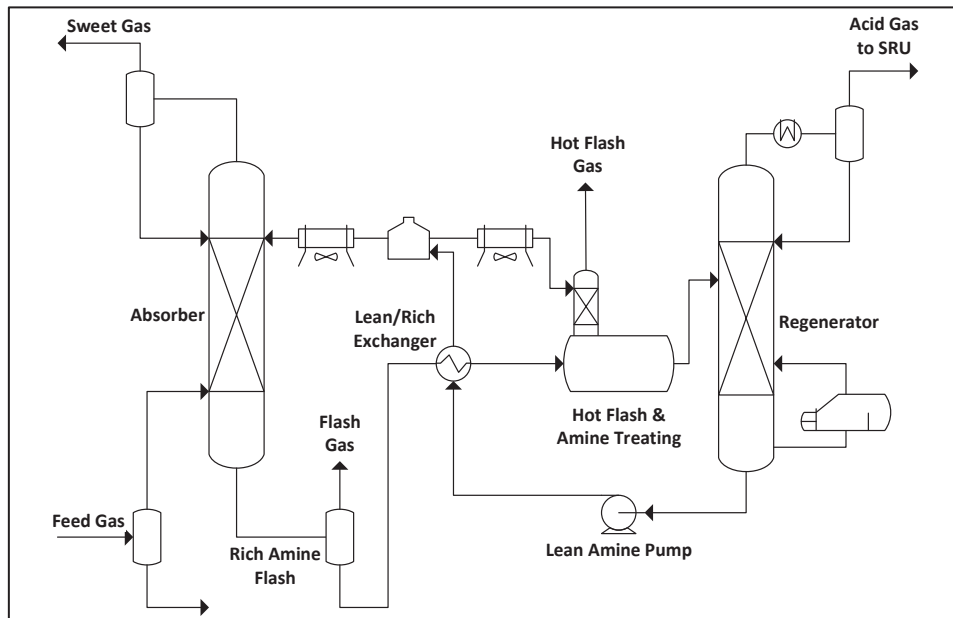
- **Option 5. Technological Solutions**

More stringent legislation has led to additional treatments being proposed in order to meet current and future environmental specifications. One proposed option is the addition of a stripping column for hydrocarbons on the rich amine line downstream of the flash drum (see Figure 11). This design uses a portion of the sweet gas to strip VOC and BTEX from the amine. A VOC and BTEX removal of greater than 75% is apparently possible, however, some  $\text{H}_2\text{S}$  and  $\text{CO}_2$  will also be stripped along with the hydrocarbons, so that stream will need to be routed to another low pressure contactor (GRU2 most likely).

Another option is a hot flash vessel (see Figure 12) that is located downstream of the lean-rich heat exchanger on the rich amine stream. Essentially, a higher temperature flash leads to more hydrocarbons being removed. The simulations show that this is more effective at removing VOCs and does not have a significant impact on BTEX. Unfortunately, substantial amounts of  $\text{CO}_2$  and  $\text{H}_2\text{S}$  are liberated at these temperatures with the VOCs requiring an additional amine contactor for these gases.



**Figure 11. Amine Plant with Hydrocarbon Stripping Column**



**Figure 12. Amine System with Hot Flash Vessel**